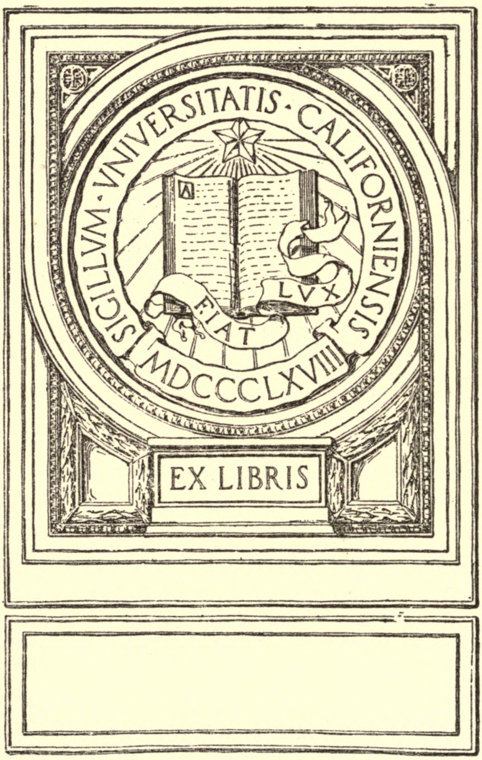

SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
FIAT LVX
MDCCCLXVIII
EX LIBRIS

4

TREATISE ON
GENERAL AND INDUSTRIAL
INORGANIC CHEMISTRY

ALSO BY DR. MOLINARI

TREATISE ON
GENERAL AND INDUSTRIAL
ORGANIC CHEMISTRY
SECOND EDITION

TRANSLATED BY
T. H. POPE, B.Sc., F.I.C., A.C.G.I.

TREATISE ON
GENERAL AND INDUSTRIAL
INORGANIC CHEMISTRY

BY

DR. ETTORE MOLINARI

PROFESSOR OF INDUSTRIAL CHEMISTRY AT THE ROYAL MILAN POLYTECHNIC
AND AT THE LUIGI BOCCONI COMMERCIAL UNIVERSITY AT MILAN

SECOND EDITION

TRANSLATED FROM THE FOURTH REVISED AND AMPLIFIED ITALIAN
EDITION BY

THOMAS H. POPE, B.Sc., F.I.C., A.C.G.I.

WITH 328 ILLUSTRATIONS IN THE TEXT
AND TWO PHOTOTYPE PLATES

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET
1920

Printed in Great Britain

TRANSLATOR'S PREFACE

In this translation the original text has been adhered to as faithfully as possible, even where the views or explanations of the author are not such as would meet with unqualified acceptance by all chemists. Where it seemed especially desirable a *Translator's Note* has been interpolated as such.

Prices have generally been given in English currency per ton, where the substance in question is sold in large quantities, and in English currency per kilogram in the case of fine chemicals; the pound sterling has been taken as equivalent to twenty-five lire.

Temperatures are always given in Centigrade degrees, and it has not been considered necessary to add the abbreviation "C." In the case of other abbreviations for units of volume, mass, etc., the abbreviations in the Chemical Society's and Society of Chemical Industry's recognised Journals have usually been followed.

The decimal system of weights and measures has been retained throughout, the decimal and English tons being practically identical for the purposes for which they are used in this work.

Thomas H. Pope.

PREFACE TO THE FOURTH ITALIAN EDITION

The third (Italian) edition of this book has been completely exhausted for more than a year, but the labour caused by the European War, which has pressed hard upon all chemical industries, has delayed the work involved in its re-issue.

The problem of the war, which in all countries has proved to be eminently chemical in character, shows how much the governments of certain nations are to blame for their past neglect of the development of the teaching of chemistry and of its modern applications. At the same time their fault would be none the less grave if their present experiences cause them to regard our science merely as an instrument for the preparation of monstrous devices destined to the work of destruction and carnage.

When mankind, which is paying with its blood for the criminal follies of the ruling classes, ceases to be deceived by the attractive, idealistic veneer masking the true fundamental ends of every war, then will chemistry no longer be a tool of barbarism, but will direct its wonderful activity to the improvement of the material and intellectual welfare of man throughout the world, irrespective of race.

The delay in the completion of the present edition is due partly to the disturbance and excitement of the war and partly to the fact that the prodigious development of industrial chemistry during the past four years has emphasised the necessity of developing chemical teaching more and more along the lines of its practical applications.

For these reasons and also because general and special treatises on chemical theory are numerous and those on chemical technology rare, I have endeavoured in this fourth edition to treat the material still more from the industrial standpoint.

Various chapters have therefore been considerably enlarged, certain improvements—presumed or real—being indicated only by the numbers of the patents in question, so that the further details may be ascertained from the journals of applied chemistry.

This edition will serve also for the second English edition.

THE AUTHOR.

MILAN.

PREFACE TO THE THIRD EDITION

In this new edition almost all the more important chapters of the book have been revised. Thus certain sections, such as those on cement, superphosphates, the utilisation of atmospheric nitrogen, white lead, steel, and water (including appendix at the end of the volume), have been considerably amplified on account of the practical and theoretical importance of these subjects, which increases daily. The chapter on cement, for example, may be useful in giving some idea of the various chemical, mechanical, and economic problems which are to-day involved in chemical industry on a large scale.

The statistics have been brought up to date so that they may offer to the reader a summary, which is sometimes very suggestive, of the progress and circumstances of the principal chemical industries of Italy and other countries.

In this third edition various analytical methods of testing the more important chemical products have been included and, in addition, numerous patents have been cited, because, apart from the new processes or new practical successes which are often embodied in them, they always contain a new idea which tends to advance the progress of chemistry in its practical applications. In these references we have cited the German patents by preference because, as is well known, these are controlled by a special technical commission, which, with rare exceptions, ensures that they are to be taken seriously, an assurance which is often wanting in the patents granted by other countries without any such guarantee.

The book thus amplified will perhaps be better capable of enabling the young chemist to prepare himself for practical activity, and may stimulate those engaged industrially, who are somewhat slower in accepting the results of chemical progress, to advance with a more eager stride.

The Author.

PREFACE TO THE FIRST EDITION

During the last century chemistry has been one of the most powerful factors of progress, civilisation, and improvement in all countries, some of which have derived from its study most important sources of wealth and activity. Germany is still benefiting from the beneficent impulse given by Liebig to chemical studies, and it was in Germany that the chemists of other countries studied their science in that school to which Liebig, Hofmann, and Kekulé gave a scientific and entirely theoretical impulse.

Nowadays, however, this mode of study does not correspond with modern requirements, because industrial problems have become specialised and intensified to such an extent, under the impulse of constant progress from day to day and the pressure of strenuous international competition, that pure theory encounters grave difficulties in finding a path through the complex and multiform organism of modern chemical industry. It is therefore necessary to-day to recognise, in general treatises at least, the more salient, marvellous, and brilliant methods which permit one to pass rapidly from the more abstract theoretical conceptions to the more important practical applications.

The young chemist should be initiated with much care into those exercises which link together theory and practice.

This necessity has led chemical teaching in a new direction.

General chemistry can no longer be a simple and arid exposition of fundamental laws and of the properties of the innumerable known substances, but should possess a soul which brings it into contact with the vital activities around which it clings. In a course of general inorganic chemistry all the applications which have been made of the fundamental laws and of the properties of substances should be studied. The chemical text-books which have been used up to the present time do not correspond sufficiently with these requirements, and it is only since a couple of years ago that attempts have been made to reform this state of affairs and to carry into practice the improvements which have been urgently demanded from several quarters.

In 1903 the University of Berlin prescribed an examination in applied chemistry even for the students of pure chemistry, and in Italy, Gabba at the Chemical Society of Milan, Cannizaro at the Chemical Congress at Turin in 1902, and Ciamician in his inaugural discourse to the students at the University of Bologna in 1904, have emphasised the urgent necessity of modifying the character of university chemical studies by special consideration of practical applications.

The author came to the same conclusions two years ago, when he was charged with the arrangement of a general course of inorganic chemistry at the Milan Polytechnic, as he had taken special notice, during several years of industrial activity, of the almost general lack of success of our young chemists when faced with practical applications of chemistry, an insuccess which explains the slow progress and sometimes even the ruin of many Italian chemical industries. Our young chemists themselves cannot be blamed for this lack of success, which is due to the erroneous direction of their training

If anything is to be attempted in Italy it should not be an imitation of what has been done in other countries in the past, but should start at the point at which other countries have arrived in order to proceed further and profit by the experience of others.

The present treatise took its rise from these considerations, and has no other pretensions than to be an attempt to initiate a work of reform in the teaching of chemistry in the hope that others may follow and carry out its objects better.

The first sections of the work are devoted to a short historical sketch of the progress of chemistry, which may perhaps be of interest to students, inasmuch as this branch of chemistry is ordinarily very incompletely or even incorrectly treated in text-books.

I have prefaced the special and systematic portion by a theoretical portion, which explains the principal fundamental laws. This portion is not especially suited for the instruction of those completely ignorant of chemistry, but appears to me, on the other hand, to offer advantages to those students of secondary institutions who have already an elementary knowledge of chemistry gained during their previous studies in high schools and technical institutes.

In the development of the descriptive portion, I have often turned back to the more important fundamental laws and completed their elucidation as well as possible. Thus the exposition of the phase rule is illustrated and completed in the chapter on sulphur, and the laws of mass action are illustrated in the section on the manufacture of catalytic sulphuric acid, and are again referred to at various other points.

The third portion, which deals with the metals, is preceded by a section on the fundamental laws of electro-chemistry and by an amplification of the electrolytic theory of solutions.

The book closes with a short summary of the periodic system of the elements.

In the special portion I have always endeavoured to emphasise very briefly those industrial processes which deal with the preparation of the more common compounds. In the case of some of those which take part in large-scale industrial operations, I have treated them rather more extensively in order to impart an idea of the character which the more important applications of chemistry assume in practice. I have done this in the case of hydrogen, which is destined to have an important industrial future, in the case of water in its very varied uses, of sulphuric acid, soda, chemical fertilisers, etc.

By means of the ordinary text-books it is difficult for the student to form a conception of the greater or lesser importance of any one compound compared with others. Many, for example, do not know whether arsenious anhydride has other applications than that of destroying rats or that other more tragic one which solves many intricate human problems; whether phosphorus has other uses than for the heads of matches, or whether hydrogen serves other purposes than the inflating of balloons. I have endeavoured to indicate as completely as possible the varied applications of each substance, and have summarised their present and past importance by means of statistics. In the case of each substance I have indicated its commercial price without any desire to offer a commercial price-list of chemical products, but merely for the sake of orientation, as quite often it is not known whether a cubic metre of oxygen costs 2*d.* or 4*s.*, whether ammonia costs more or less than nitric acid, copper more or less than aluminium or nickel, etc. In general nothing is available with regard to the prices of chemical products but the fantastic price-lists of the pharmacists.

I have purposely omitted the description of ordinary laboratory apparatus, because this is of subsidiary importance for the student, and serves only as an aid to the professor in imparting knowledge, and may be found in special works. I have substituted for this cumbersome material simple and illuminating sketches of industrial apparatus and processes which I have collected from the best works on chemical technology (Muspratt, Dammer, Bertsch, Lunge, etc.) from patents or directly from practice in works which I have visited in Italy and other countries.

Thus the student will become accustomed to comprehend those means by which processes pass from the experiments of the school and from more abstract scientific considerations to the more important industrial applications. Practical disappointment and disastrous failure, due to too dogmatic and simple conceptions acquired during the teaching of the schools, will be spared to many in the future. They will learn how one passes from the retort and the beaker to the more wonderful devices of modern technology, and how in the course of chemical processes in practice one must take into account not only the main reactions which are ordinarily found in the books, but also the secondary reactions, special conditions of temperature, pressure and time, and the proportions of the reacting substances. These are all conditions which may decide the success or failure of an entire industry.

I am far from believing that this book may be considered as a treatise on chemical technology, but it is my conviction that industrial chemistry must start from the foundations of general chemical culture embodied in this treatise, then to enter into all the technical and economic conditions of manufacture of the more important compounds and to place the young chemist in a position to assume the direction of and collaboration in our chemical industry with more success and utility.

THE AUTHOR.

MILAN, *September* 1904.

CONTENTS

PAGE

TRANSLATOR'S PREFACE v

PREFACE TO THE FOURTH EDITION vii

PREFACE TO THE THIRD EDITION viii

PREFACE TO THE FIRST EDITION ix

PART I. GENERAL

MATTER, SPACE, SUBSTANCE, MASS 1

PHYSICAL AND CHEMICAL PHENOMENA. Conservation of energy . . 2

HISTORY OF CHEMISTRY. From the ancient Chinese to Lavoisier . . 9

FUNDAMENTAL LAWS OF MODERN CHEMISTRY. Law of constant proportions : Equivalents : Law of multiple proportions 19

LAWS OF MATTER IN THE GASEOUS STATE. Boyle's Law : Law of Gay-Lussac and Dalton : Absolute units : Critical temperatures and pressures of gases : Liquefaction of permanent gases : Laws of Gay-Lussac on gaseous combination : Avogadro's Law : Determination of the densities of gases and vapours : Kinetic theory of gases : Bunsen's effusiometer : Exceptions to Boyle's Law : van der Waals' new equation : Size of the molecules : Chemical symbols and formulæ : Table of atomic weights : Dualistic formulæ : Valency : Monatomic molecules : Thermal capacity and specific heat of gases : Principles of thermodynamics : Optical properties of gases : Spectroscopy 23

CHEMICAL EQUATIONS. THERMOCHEMISTRY. Rule of antitheses : Chemical equilibria and velocities of reaction : Reversible reactions : Catalytic phenomena : Affinity : Solubility of gases in liquids and in salt solutions 59

MATTER IN THE LIQUID STATE. Specific gravity : Pyknometers : Mohr's balance : Hydrometers : Specific heat of liquids and solutions 75

STUDY OF DILUTE SOLUTIONS. Osmotic pressure : Surface tension of liquids : Vapour pressures of solutions : Molecular weights : Ebullioscopy : Freezing-point of solutions : Cryoscopy : Anomalies in cryoscopy and ebullioscopy : Relation between vapour pressure and osmotic pressure : Molecular weight deduced from the action of two solvents on a single substance : Electrolytic dissociation of solutions : Ionic theory : Double decomposition of salts : Analytical tests for ions : Valency of ions : Normal solutions and volumetric analysis : Indicators : Heat of formation of ions : Degree of dissociation, equivalent conductivity, specific conductivity : Isohydrism and equilibrium between ions : Mobility of ions and transport numbers : Colour of ions : Ions and electrons : Colloidal solutions : Ultramicroscopy 80

MATTER IN THE SOLID STATE. Specific gravity : Specific heat : Matter in the crystalline state : Isomorphism : Liquid crystals : Equilibrium in heterogeneous systems and the phase rule : Radium, radio-activity, and unity of matter 111

PART II. SPECIAL PART

PAGE

CLASSIFICATION OF THE ELEMENTS 133

HYDROGEN. Properties : Uses : Preparation in the laboratory : Industrial preparation : Analysis 133

NON-METALS. Halogen group. FLUORINE : Properties : Preparation . . 147

CHLORINE. Properties : Applications and statistics : Laboratory preparation : Industrial methods : Liquid chlorine : Analysis 149

BROMINE. Properties : Applications : Statistics : Preparation, both in the laboratory and industrially 158

IODINE. Properties : Uses : Statistics : Industrial preparation : Analysis . . 161

HYDROGEN COMPOUNDS OF THE HALOGENS. Hydracids : HYDROFLUORIC ACID : Properties : Applications : Industrial preparation : Analytical tests . 166

HYDROCHLORIC ACID. Properties : Uses : Preparation : Industrial methods : Legislation on hydrochloric acid manufacture : Purification : Table of specific gravities : Analytical tests 169

HYDROBROMIC ACID. Properties : Uses : Preparation 181

HYDRIODIC ACID. Properties : Uses : Preparation 182

COMPOUNDS OF THE HALOGENS WITH ONE ANOTHER. Iodine chloride : Iodine trichloride : Iodine bromide : Iodine pentafluoride 184

OXYGEN COMPOUNDS OF THE HALOGENS. Hypochlorous anhydride : hypochlorous acid : Chlorine dioxide and tetroxide : Chloric acid : Perchloric acid 184

OXYGEN GROUP. OXYGEN : Properties : Uses : Sale : Preparation : Industrial processes : ACTIVE OXYGEN 187

OZONE. Formation : Properties : Liquid ozone : Characteristic reactions : Applications : Industrial preparation : Analysis : Antiozone 199

SULPHUR. Properties : Precipitated sulphur : Uses : Commercial varieties : Statistics : Extraction : Native sulphur : Refining : Ground sulphur : Analysis . 205

SELENIUM and TELLURIUM : Properties 220

HYDROGEN COMPOUNDS OF THE GROUP : OXYGEN, SULPHUR, SELENIUM, TELLURIUM 222

WATER. Properties : Table of vapour pressures, temperatures, and densities : Drainage water : River water : Lake water : Sea water : Potable water : Cisterns : Wells : Aqueducts : Analysis : Purification : Filtration : Sterilisation : Water for Industrial Uses : Elimination of iron from ferruginous waters : Purification of effluent waters : Distillation of sea water : Distilled water : Natural and artificial mineral waters : Freezing mixtures : Natural and artificial ice : Refrigerating industry : Applications of cold : Statistics 222

HYDROGEN PEROXIDE. Properties : Uses : Preparation 266

HYDROGEN SULPHIDE. Properties : Uses : Preparation : Hydrogen persulphide : Hydrogen selenide : Hydrogen telluride 270

HALOGEN COMPOUNDS OF SULPHUR. Sulphur chloride, dichloride, and tetrachloride 273

OXYGEN COMPOUNDS OF SULPHUR, SELENIUM, AND TELLURIUM . 274

Salts, Acids, and Bases : Nomenclature 274

PAGE

SULPHUR DIOXIDE. Properties : Uses : Statistics : Industrial preparation. SULPHUROUS ACID. HYDROSULPHUROUS ACID. SULPHUR SESQUIOXIDE . . . 275

SULPHURIC ACID. Properties : Uses : Table of densities : Resistance of metals : Statistics : Theory of the formation of sulphuric acid in the lead chambers : Preparation : Pyrites : Pyrites burners : Sulphur burners : Lead chambers : Plate towers : Gay-Lussac towers : Concentration : Purification : Analytical tests : Yields 282

SULPHUR TRIOXIDE. Properties : Fuming sulphuric acid : Table of densities of oleum : Industrial preparation 314

DERIVATIVES OF SULPHURIC ACID. Persulphuric acid : Caro's acid : Thiosulphuric acid : Polythionic acids : Dithionic acid : Trithionic acid : Tetrathionic acid : Pentathionic acid : Chloroanhydrides : Monochloroanhydride : Dichloroanhydride : Amino derivatives : Sulphamide : Sulphimide 328

OXYGEN COMPOUNDS OF SELENIUM AND TELLURIUM. Selenium dioxide : Selenious anhydride : Selenic acid : Tellurium dioxide : Telluric acid 331

NITROGEN GROUP. NITROGEN : Properties : Preparation 331

ATMOSPHERIC AIR 334

LIQUID AIR. Preparation : Application : Oxyliquit : Processes of Linde, Claude, and Pictet 338

UTILISATION OF ATMOSPHERIC NITROGEN. Biological process : Electrical process : Chemical processes 347

NEW GASES. ARGON : HELIUM : NEON : KRYPTON : XENON 351

AMMONIA. Properties : Industrial preparation : Ammonia from illuminating gas : Other sources of ammonia : Ammonia from coal, etc. : Mond gas producer : Synthetic ammonia : Calcium cyanamide : Analytical tests : Liquid ammonia : Statistics and uses 353

HYDROGENATED AND HALOGENATED NITROGEN DERIVATIVES. Hydrazine and its hydrate : Azoimide or hydrazoic acid : Hydroxylamine : Nitrogen chloride : Nitrogen iodide : Azoimide iodide 376

OXYGENATED COMPOUNDS OF NITROGEN. Nitrous oxide : Hyponitrous acid : Nitric oxide : Nitrosyl chloride : Nitrogen trioxide : Nitrous acid : Nitrosylsulphuric acid : Nitrogen peroxide : Nitrogen tetroxide and dioxide : Nitric anhydride 377

NITRIC ACID. Properties : Table of densities : Industrial preparation : Continuous processes : Sodium bisulphate : Synthetic nitric acid : Concentration : Fuming nitric acid : *Aqua regia* : Pure nitric acid : Uses of nitric acid : Quantitative analysis : Prices and statistics 383

PHOSPHORUS. Properties : Preparation : Dippel animal oil : Animal charcoal : Red or amorphous phosphorus : Black phosphorus : Uses of phosphorus : Match industry : Statistics of matches : Statistics of phosphorus 402

HYDROGEN PHOSPHIDE. Phosphonium iodide, chloride, and bromide : Liquid and solid hydrogen phosphide 410

THERMOCHEMICAL BEHAVIOUR OF HALOGENATED PHOSPHORUS DERIVATIVES. Phosphorus trichloride : Phosphorus pentachloride : Bromides and iodides : Penta- and tri-fluorides 412

OXYGENATED AND HALOGENATED PHOSPHORUS COMPOUNDS. Oxides : Acids : Phosphorus suboxide : Trioxide : Tetroxide : Phosphoric anhydride : Hypophosphorous acid : Metaphosphoric acid : Phosphorous acid : Phosphoric acid : Metaphosphoric acid : Pyrophosphoric acid : Hypophosphoric acid . . 413

PAGE

VARIOUS PHOSPHORUS COMPOUNDS. Oxychloride : Sulphochloride : Trisulphide : Pentasulphide 418

ARSENIC. Hydrogen arsenide : Arsenic disulphide : Trisulphide : Pentasulphide : Thiosalts : Thioarsenates : Chlorides : Iodides 418

OXYGEN COMPOUNDS OF ARSENIC. Arsenic trioxide : Arsenious acid : Arsenic pentoxide : Arsenic acid 423

ANTIMONY. Properties : Preparation : Uses and production : Statistics : Explosive antimony : Hydrogen antimonide : Antimony trichloride : Pentachloride : Fluoride : Oxygen compounds : Sulphur compounds : Cinnabar of antimony : Sodium thioantimonate 426

VANADIUM : COLUMBIUM : TANTALUM 433

CARBON GROUP 435

CARBON. Diamond : Graphite : Statistics of graphite 435

FUEL. Origin and composition of coal : Peat : Lignite : Coal : Table of production and consumption : Anthracite : Coke : Metallurgical coke : Wood charcoal : Animal charcoal : Briquettes : Lamp-black : Coal as a source of heat : Flameless combustion : Nature of flame : Thermal balance in the fusion of metals and alloys 441

CARBON COMPOUNDS. Tetrachloride : Tetra-iodide : Dioxide : Properties : Applications : Industrial preparation : Solid carbon dioxide : Statistics . . . 469

CARBON MONOXIDE. Preparation : Water gas : Producer gas : Suction gas : Carbon suboxide : Nickel tetracarbonyl : Carbonyl chloride : Carbonyl nitride : Carbon disulphide : Carbon monosulphide : Trithiocarbonic acid : Carbon oxysulphide : Cyanogen compounds : Hydrocyanic acid 484

SILICON. Silicon compounds : Tetrachloride : Fluoride : Carbide : Calcium silicide : Silica : Silicon monoxide : Silicic acid : Disulphide : Nitride 497

TITANIUM. Chloride : Dioxide : Peroxide : Titanic acid 502

ZIRCONIUM 503

THORIUM. Thorium nitrate : Chloride : Hydroxide : Rare earths for incandescent lighting 504

BORON. Boron hydride : Boric anhydride : Boric acid : Halogen derivatives of boron 506

PART III. METALS

METALS. Table of physical constants : Metallic alloys 511

ELECTROCHEMISTRY. E.M.F. of metals : Voltaic series of the elements : Electrolysis : Accumulators : Valency of metals 518

GROUP I

ALKALI METALS 527

POTASSIUM. Potassium salts and fertilisers : Hydride : Oxide : Potassium salts and the European War : Hydroxide (caustic potash) : Potassium chloride : Bromide : Iodide : Fluoride : Hypochlorite : Chlorate : Perchlorate : Nitrate (nitre, saltpetre) : Nitrite : Sulphate : Bisulphate : Persulphate : Sulphite and bisulphite : Sulphide : Hydrogen sulphide : Polysulphides : Carbonate : Bicarbonate : Percarbonate : Silicate : Trithiocarbonate : Cyanide : Phosphates : Characteristic reactions of potassium salts 527

PAGE

Rubidium. Caesium 551

Sodium. Oxide : Peroxide : Sodamide : Hydroxide : Specific gravities of sodium and potassium hydroxide solutions : Processes of manufacture : Concentration of caustic soda solutions : Applications, statistics, and prices : Analysis of sodium hydroxide : Sodium chloride : Production : Industrial denatured salt : Bromide : Iodide : Chlorate : Perchlorate : Iodate 551

Alkali Hypochlorites. Bleaching salts : Sodium nitrate : Importation from Chile : Analysis of nitrate : Sodium nitrite : Sodium sulphate : Analysis : Bisulphate : Pyrosulphate : Sulphite : Bisulphite : Thiosulphate : Hydrosulphite : Pyrosulphite : Persulphate : Sulphide : Sodium Carbonate : Specific gravities of sodium and potassium carbonate solutions : Leblanc process : Ammonia soda process : Cryolite process : Electrolytic process : Statistics : Sodium bicarbonate : Analysis of soda : Sodium phosphates : Borate : Perborate : Silicate : Azide : Cyanide : Reactions of sodium salts 572

Lithium. Chloride : Hydride : Phosphate : Carbonate 607

Ammonium. Chloride : Chlorate : Perchlorate : Fluoride : Sulphate : Table of production : Nitrate : Nitrite : Hyponitrite : Carbonate : Phosphates : Sulphide : Hydrosulphide : Reactions of ammonium salts 608

GROUP II

Alkaline Earth Metals 614

Calcium. Nitride : Hydride : Oxide : Quicklime : Hydroxide : Slaked lime : Peroxide : Soda-lime : Carbonate : Chloride : Table of freezing-points of brines : Bromide : Fluoride : Hypochlorite : Nitrate : Nitrite : Sulphide : Sulphite : Sulphate : Silicate : Glass : Raw materials for glass manufacture : Glass manufacture : Statistics : Calcium carbide : Phosphates 614

Chemical Fertilisers. Superphosphates : Mineral phosphates : Basic slag : Theory of superphosphate manufacture : Industrial processes : Superphosphates without sulphuric acid : Production of phosphorites : Phosphorite industry : Exportation of phosphorites 643

Strontium. Oxide : Hydroxide : Peroxide : Chloride : Nitrate : Sulphate : Carbonate 662

Barium. Oxide : Hydroxide : Peroxide : Chloride : Nitrate : Sulphate : Sulphide : Carbonate 663

Hydrazine 668

MAGNESIUM SUB-GROUP 668

Magnesium. Asbestos : Oxide : Peroxide : Hydroxide : Chloride : Sulphate : Carbonate : Phosphates : Silicates : Talc : Nitrate : Nitride 668

Glucinum. Oxide : Hydroxide : Chloride : Carbonate : Sulphate 675

Zinc. Zinc ores : Electrolytic processes : Oxide : Peroxide : Hydroxide : Chloride : Sulphate : Hydrosulphite : Carbonate : Sulphide : Lithopone : Phosphide . 675

Cadmium. Oxide : Hydroxide : Chloride : Sulphate : Sulphide 684

Mercury. Properties : Mercurous compounds : Mercuric compounds . . . 684

GROUP OF COPPER, SILVER, AND GOLD 691

Copper. Output of ore : Treatment of ore : Refining : Chlorination : Electrolytic process : Alloys : Statistics. Cuprous Compounds : Cupric Compounds : General reactions of copper salts 691

PAGE

SILVER. Extraction with lead : Other methods of extraction : Properties : Statistics : Oxides : Chloride : Bromide : Iodide : Fluoride : Nitrate : Nitrite : Sulphite : Sulphate : Azide : Photographic process : Catatype process 707

GOLD. Refining : Properties : Production. AUROUS COMPOUNDS. AURIC COMPOUNDS Gold salts 717

GROUP III. TRIVALENT METALS

ALUMINIUM. Properties : Uses : Alumino-thermic welding : Statistics : Compounds : Oxide : Hydroxide : Chloride : Sulphate : Alums : Statistics on alums : Silicates : Ceramic industry : Porcelain : Constructive materials : Bricks and artificial stone : Statistics on kaolin : Hydraulic mortars : Cements : Natural and artificial cements : Roman cement : Portland cement : Theory of setting and hardening : Grinding : Kilns : Rotary kilns : Cement testing : Reinforced concrete : Statistics : Table of production : Ultramarine 723

GALLIUM : INDIUM : THALLIUM 772

ELEMENTS OF THE RARE EARTHS : SCANDIUM : CERIUM : LANTHANUM : PRASEODYMIUM : NEODYMIUM : YTTERBIUM : YTTRIUM : SAMARIUM 773

GROUP IV. TETRAVALENT METALS

GERMANIUM. Oxide : Sulphide 775

TIN. Properties. STANNOUS COMPOUNDS. STANNIC COMPOUNDS. Mosaic gold . 776

LEAD. Extraction : Roasting : Refining : Properties : Statistics : Compounds : Oxides : Hydroxide : Minium (red lead) : Dioxide : Chloride : Tetrachloride : Iodide : Nitrate : Sulphates : Carbonates : White lead : Properties : Sulphide : Arsenate 782

GROUP V

BISMUTH. Alloys : Theory of the melting-point of alloys : Chloride : Suboxide : Trioxide : Dioxide : Hydroxides : Bismuthic acid : Nitrate : Sulphide . . 792

GROUP VI

CHROMIUM. Hydroxide : Oxide : Chlorides : Fluoride : Sulphate : Alums : Chromic acid derivatives : Chromic anhydride : Alkali chromates and dichromates : Perchromic acid : Chrome alum 794

MOLYBDENUM 799

TUNGSTEN. Properties : Uses : Statistics : Derivatives 799

URANIUM. Oxides 803

GROUP VII

MANGANESE. Statistics : Oxide : Hydroxide : Chloride : Sulphate : Sulphide : Carbonate : Persulphate : Derivatives of manganic and permanganic acid : Potassium permanganate : Permanganic anhydride 804

GROUP VIII

IRON. Properties : Metallurgy : Cast-iron : Wrought-iron : Electrolytic iron : Steel : Bessemer process : Martin (open-hearth) process : Electric processes : Uses and properties of different steels : Ferrosilicon : Ferromanganese : Micrography : Ferrite : Graphite : Cementite : Pearlite : Martensite : Austenite : Troostite : Sorbite : Production of cast-iron and steel : Tungsten steel : Silicon steel : Statistics 809

PAGE

FERROUS COMPOUNDS. FERRIC COMPOUNDS. Pyrites : Cyanogen compounds of iron : Ferrocyanides : Thiocyanates : Prussian blue : Ferricyanides : Black prussiate 836

NICKEL. Galvanoplastics and electro-plating : Statistics : Oxides : Sulphates : Sulphides : Nickel tetracarbonyl : Cyanide 844

COBALT. Oxides : Hydroxide : Nitrate : Silicate : Nitrite : Complex ammonium salts : Werner's theory 846

PLATINUM GROUP. Ruthenium : Rhodium : Palladium : Osmium : Osmium oxides : Iridium 849

PLATINUM. Statistics and Prices : Chlorides : Cyanide 852

PERIODIC SYSTEM OF THE ELEMENTS. Table 854

INDEX 859

PART I. GENERAL

Everything which exists, everything which directly or indirectly influences our senses, constitutes Nature or the universe, of which we ourselves form part.

It is now assumed that the one fundamental essential constituting Nature is none other than Energy, which, in various qualities and in its many transformations and combinations, also changes into those well-defined forms which constitute the innumerable substances of the universe.

Bodies formed of one or more substances influence one another reciprocally in various ways, and the perception of their forms and their properties is all relative to the nature of the organism influenced by them. Thus the forms and qualities which we perceive in the bodies around us are relative to our sensitive faculties or to the special constitution of our organism, but there is nothing to prove that these bodies have, in any absolute sense, the forms and properties which we attribute to them.

If we consider abstractly imaginary organisms quite different from ourselves or from members of the animal kingdom to which we belong, then the nuclei of energy which constitute bodies as we know them will manifest themselves to these hypothetical organisms in quite a different shape and manner.

These abstract considerations do not, however, modify the methods of perception of nature by the human organism, so that all the researches and all the deductions and victories of the natural sciences retain a general and positive value for mankind.

The distinction which was once made between matter and energy is not rigorous and has been generally abandoned in favour of the more general conception of energy as the sole real entity.[1]

A *body* is a part of space in which there are indissolubly united certain quantities of energy of distance (*weight*), energy of motion (*mass*), and energy of volume (*volume*).

Bodies are formed of various *substances*, which are in their turn manifestations of chemical energy, variously grouped in different compounds and distinct from other forms of energy by which, however, they are usually accompanied

---

[1] In fact, if we analyse the inner nature of matter we must at once admit that we perceive the objects of the external world (and we may add that we acquire consciousness of our own existence) solely in virtue of the influence exercised by these objects on our senses. Now the causes of our perceptions are the qualities and properties (due to various forms and differences of energy) which we consider to be inherent to matter (light, the various colours and physical state are all forms of energy); but if we for a moment imagine matter divested of all these properties in order to see what remains, we find that there is nothing perceptible, that is to say, we cannot then demonstrate the existence of matter. That energy alone should exist, without matter, would appear to be a contradiction of the law of gravitation, to which matter itself is said to be subject; but gravitation is merely a form of energy, which can only manifest itself by contrast with other forms of energy. In fact gravitation is, more exactly stated, energy of distance.

In ordinary language the use of the word matter is so well established that it is impossible always to avoid its use, but this does not invalidate what we have said above.

(thermal, electric, mechanical, and radiant energy, etc.); the magnitude of this chemical energy is measured by the product of two inseparable factors, the factor of capacity (*mass*)[1] and the factor of intensity (*chemical affinity* or *chemical potential*, which is the cause of all chemical reactions).

The specific properties of substances are represented by the quotient of two factors, intensity and capacity.

Bodies are distinguished from one another by variable properties only (form, magnitude, etc.); thus, for example, a cube of sugar is a body, because it has an inherent, well-determined form, that of the cube, which constitutes a variable property, because the cube may be more or less large. The component—sugar—on the other hand, is a substance with well-defined and invariable specific properties. In fact, on breaking up the cube, the sweet taste characteristic of sugar still remains, and this property does not disappear even when the sugar is dissolved in water.

Thus, again, a beaker, mirror, bottle, etc., are all bodies, very distinct from one another in form and size, but all constituted of the same material, glass, with invariable specific properties.

The descriptive natural sciences, botany, anatomy, zoology, crystallography, etc., study more especially the internal and external forms of bodies, whilst the speculative natural sciences, physics and chemistry, mainly study substances through their specific properties, transformations and combinations.

More exactly, physics is the study of all the modifications in properties which substances can undergo without durably losing any of their specific properties, that is to say, without being transformed into other substances.

Chemistry, on the other hand, studies the stable modifications of the properties of substances when these lose any of their specific properties and acquire others; that is, when they are transformed into other substances.

On heating water to 100° it is transformed into steam, which, in turn, is reconverted into water when cooled and condensed; in this case the water has not undergone any essential modification. If we heat in a bulb a fragment of a substance of metallic aspect called iodine, we obtain violet vapours, which recondense on cooling on the sides of the bulb in scales of iodine, lustrous as before, showing that the iodine has not lost its intrinsic qualities by changing its form and state. A platinum wire, when heated, becomes red and glowing, but is still always platinum, and is found to be unaltered on cooling. When sulphur is heated out of contact with the air it becomes liquid and of a reddish colour; on raising the temperature it again becomes solid, and finally liquid again at a still higher temperature; if it is poured into water when in this condition it becomes solid, but is at first plastic, and only becomes hard and friable, as it was originally, after some time. During all these long and various transformations the substance has not been altered; the sulphur always remains sulphur. If fine zinc filings and flowers of sulphur are mixed, an apparently homogeneous mass is obtained, which differs in appearance from its components. But with a simple lens the constituents are easily distinguished, and on pouring the mass into water the zinc is readily separated from the sulphur, as the latter remains on the surface, whilst the former sinks to the bottom. Thus also from a mixture of iron filings and sulphur the two components are easily separated with a magnet.

The experiments which have just been enumerated all illustrate so-called *physical phenomena*.

If, on the other hand, we take the mixture of zinc and sulphur, made in

---

[1] Whilst all the masses concerned in the various forms of mechanical energy are equivalent and homogeneous, in chemical energy the masses are of varying nature and characterise the various simple substances (elements).

certain definite proportions, and heat it in a dish, it catches fire, producing much heat and light, and we obtain a new white, voluminous substance which, when examined with a lens, poured into water, or investigated in any other way, cannot be separated into particles of the two components. Thus a new substance has been formed which no longer has any of the specific properties of the two original substances. This is a chemical phenomenon, because the nature of the admixed substances has been changed in a stable manner, a sulphide of zinc being produced. So on heating sulphur and iron filings in a glass tube the mass glows and catches fire, and we obtain a new substance differing in a stable manner from the components, which we are not able to separate by ordinary means, such as by a magnet. On mixing together powdered tartaric acid and sodium bicarbonate an apparently homogeneous substance is obtained, though with a lens this is seen to be a mixture of crystals of the two components; on throwing this mixture into water a strong evolution of gas occurs, and the two substances are intimately combined, so that on evaporating almost all the water a product remains which is quite distinct, and nothing remains of the two components from which it has been formed.

If red mercuric oxide is heated in a test-tube a metallic mirror of mercury is formed on the walls, a gas is evolved (oxygen) which revives the combustion of a glowing splint of wood, and the mercuric oxide is completely decomposed.

If sulphur is heated in a tube without access of air, it changes its physical state, but the intimate character of the material is unaltered. If, on the other hand, sulphur is heated in a spoon, with access of air, it catches fire with a blue flame, emitting a colourless gas; the sulphur disappears, and in its place we have a colourless gas, soluble in water, which shows special reactions and reddens blue litmus paper.

On burning magnesium wire a very vivid light and a white powder of magnesium oxide are produced. On bringing ammonia vapours into contact with those of hydrochloric acid white fumes of ammonium chloride are produced.

These are all chemical phenomena.

Now that we have seen how substances are modified and transformed in many various ways we will endeavour to understand their constitution more exactly in order to be able to explain all these phenomena and many others, by passing from the simpler to the more complex.

Are substances formed of a continuous, uninterrupted mass, or are they constituted of many particles, which unite in various forms? The chemist and the physicist have answered this question by rejecting the first hypothesis and accepting the second, because by its means chemical phenomena are more easily explained, and reasons are found for the expansibility and elasticity of bodies and for the diffusion of gases, which cannot be explained on the hypothesis of continuous matter.

Matter, then, must be considered as an aggregation of very small particles, extremely close together, but entirely distinct from one another. The finest particles of the most impalpable powder are enormously larger than those imagined by the chemist and the physicist.

A very simple experiment which will give an approximate idea of the smallness of these chemical particles is the following: 1 mgm. of Rhodamine Extra (an artificial red dyestuff) is dissolved in a few c.c. of alcohol and then poured into a bottle containing 10 litres of water, which is coloured red in a very evident manner. If we take a drop of this liquid, or, to be more exact, one milligram, and observe it microscopically under a magnification of 1000 diameters we find that it is still coloured red, but that there is no differentiation into coloured and colourless particles. Now 10 litres of water, that is, 10,000,000 mgms., contain 0·001 grm. of rhodamine, so that each milligram of the solution contains $\frac{0{\cdot}001}{10{,}000{,}000}$, that is, 0·000,000,000,1 grm. of rhodamine (one ten-thousand-millionth of a gram).

But if this solution is diluted 1000 times, that is, 1 c.c. diluted to one litre, and a glass tube some metres long filled with the liquid, then on illuminating the solution and looking through some depth of it, it will still appear to be homogeneously coloured, and if each milligram of this new solution contains at least one particle of dyestuff, this will weigh less than 0·000,000,000,000,1 gram., that is, less than one ten-billionth of a gram. We may also confirm this result in another manner: If we take one milligram of concentrated attar of roses, dissolve it in a little alcohol or ether, and pour the liquid over a strip of filter-paper placed on a warm plate, the room will become perfumed with the essence in a few minutes. In the case of a large room having the dimensions 35 × 12 × 7 metres, the cubical contents will be 3000 cubic metres or 3,000,000,000,000 cu. mm., which together contain one milligram of the perfume; thus 1 cu. mm. contains $\frac{0{\cdot}001}{3{,}000{,}000{,}000{,}000}$, that is, 0·000,000,000,000,000,333 grm. of perfume, so that each particle of attar of roses will certainly weigh less than one-third of a thousand-billionth of a gram. In this case the sense of smell is more sensitive than that of sight in the case of coloured solutions.

In 1905, by illuminating solutions of fluorescein with a powerful electric arc, Spring deduced that the weight of the atom of hydrogen must be less than $2{\cdot}5 \times 10^{-21}$ grms.

It is precisely with these hypothetical infinitesimal particles that chemistry is concerned, and these are the particles which we will study in the various aspects which they present to us, in their most interesting properties, forming a marvellous world, regulated by positive and eternal laws.

THE CONSERVATION OF ENERGY AND OF MASS

The principle of the conservation of energy, or equivalence of the various forms of energy, is the *first law of thermodynamics*. We have mechanical *energy* (of distance, volume, surface, and movement), and *non-mechanical energy* (chemical, thermal, electric, and radiant energy, etc.).

The value of each form of energy, as we have already seen in the case of chemical energy, is always expressed by the product of the factors of intensity and of capacity; mechanical energy is expressed by the product of mass and velocity $\left(\frac{mv^2}{2}\right.$ or *kinetic energy*$\left.\right)$; in the case of thermal energy the factor of capacity is measured by the quantity of heat expressed in calories and the factor of intensity (or thermal potential) by the temperature; for energy of distance the factors are the distance in metres and the force in kilogram-metres; for energy of volume we have volume and pressure, etc.

For each form of energy the equivalent in other forms has been established; thus we have the mechanical equivalent of heat, the electrical equivalent of mechanical energy and of heat, etc.

In many practical cases we are able to follow the equivalent transformation of the various forms of energy, but especially in the case of mechanical energy, which is present in the two reversible forms of potential energy and kinetic energy; the first is dependent on the position occupied by a body, and when its position is changed this energy is converted into kinetic energy.

If, for example, a heavy object is on the ground and we wish to raise it to a height of one metre by placing it on a support, we must perform a certain amount of work. But this work is not lost, but passes into, or accumulates in, the raised body in that form of energy which we call potential energy. We may soon prove that this energy is not lost by connecting the heavy body by means of a wire with another body of equal weight, and passing the wire over an ideal frictionless pulley, also avoiding the friction of the air. On removing the support of the upper body a minimal impulse causes the upper body to descend, but in descending it carries the lower body upwards by the pull on the wire. The first body has lost potential energy, this being transformed into energy of motion, that is, kinetic energy, which has served to raise exactly the same weight as had previously been raised by our hands. Thus we see that work has been performed by transformation of energy, which energy has not been lost but has been transformed from potential energy, that is, energy of position, into actual or kinetic energy (energy of motion).

Examples of potential energy and of its transformation into kinetic energy are very abundant.

The movement and position of the planetary systems are the most perfect examples of continuous and incessant transformation of potential and kinetic energy. A large meteorite falling and giving up all its potential energy will acquire such a velocity that on reaching the earth's surface it will collide with it in a formidable and disastrous manner. This does not ordinarily happen, because a part of the energy is given up to the atmosphere through which the meteorite is obliged to pass, with a large amount of friction, before reaching the earth's surface, and a large part of the potential energy is thus transformed into thermal energy and reduces the velocity, so that the meteorite is heated and becomes red-hot. Even the hail which forms at high altitudes would break the most resistant roofs of the houses on which it falls, if it did not impart some of its energy to the atmosphere. The potential energy of falling water produces kinetic energy in a useful and evident manner on passing between the blades of a turbine.

But in the small world of the chemical particles the cases of potential energy are extraordinarily impressive, because in chemical systems enormous quantities of potential energy, or energy of position, take part.

If the configuration of our hypothetical system of chemical particles constituting a given substance is modified and the particles change their position, giving rise to another system (another substance), when, in short, the particles at any given point under certain conditions approach one another in such a manner as to form a new substance, then the amount of potential energy which is transformed into kinetic energy is so large and powerful as to astonish the most fantastic thinker.

The particles of hydrogen gas have a velocity of about two kilometres per second, and when they approach those of oxygen under certain external influences—impelled by their great velocity—in such a manner as to attract and combine with them, the potential energy is transformed into kinetic energy so violently as to give rise to heat, light, and detonation, with formation of water, a new substance. (*Translator's note.*—The kinetic energy due to the velocity of the hydrogen and oxygen molecules is quite distinct from their potential chemical energy, which is evidenced in the combination.)

In changing the position of their particles during a chemical reaction a few grams of dynamite or nitroglycerine enclosed in the interior of a rock produce such a quantity of kinetic energy that the most resistant rock is shattered; in a few seconds an amount of work is accomplished which hundreds of workmen could not achieve in twenty-four hours.

Kinetic energy is of much interest to us, especially in its various transformations.

Matter, which we consider as divided into very small particles, manifests itself to us by means of its energy, which may be explained as an oscillatory movement of these particles, in the form of continuous, uninterrupted attractions and repulsions, these reaching our senses in the form of vibrations transmitted by the ether, which is extremely attenuated and imponderable, and fills the entire universe.[1]

---

[1] In order to explain chemical phenomena, matter has been imagined to be divided into very minute particles having a definite weight and volume. In order to explain certain physical phenomena scientists have had to make use of a hypothetical substance very much less dense than the chemical particles, so much so as to be imponderable, a substance which extends throughout the universe and penetrates all bodies, including the walls of glass vessels, etc. This substance is called the *vibratory ether* or *cosmic ether*, and is the medium by means of which the more important physical, electrical, and optical phenomena, etc., are manifested. When one remembers that solar light reaches us through space with a velocity of 300,000 kilometres per second, traversing regions where there is no air or other ponderable matter, it would be impossible to imagine such a rapid transmission without supposing the existence of the vibratory

Let us suppose for a moment, with Crookes, a long thin plate of steel, fixed in the middle of a dark room; on causing the plate to oscillate gently all its particles will vibrate, and if these vibrations exceed sixteen per second we shall observe a slight note; as the vibrations are gradually increased in frequency up to 40,000 per second, we ascend the scale of all notes from the lowest to the highest and shrillest; we have thus obtained energy of sound. If the number of vibrations is further increased they are no longer perceived by the ear, but on approaching the plate with the hand it will be observed that it is warm; we are obtaining thermal energy. If the frequency increases still further the temperature rises, and when the vibrations have attained a frequency of 400 billions per second the plate becomes red-hot and gradually more luminous; we have now luminous energy. If the frequency of the vibrations exceeds 800 billions per second our eyes are no longer able to perceive them, but if a photographic plate containing silver salts is exposed to these rays, it is affected; we have reached chemical energy, and by proceeding further it is theoretically possible to arrive at electrical energy, etc.

The transformations of kinetic energy are to-day of the greatest importance, and we see every day thousands of practical examples of the manner in which it may pass from one form to another.

Another experiment which gives some idea of the transformation of mechanical energy into thermal and luminous energy is the following: On throwing a piece of sodium into water it floats and travels rapidly over the surface, developing hydrogen gas, but if a piece of filter-paper is placed on the surface of the water and the sodium is placed on this, its motion is prevented; the energy produced, which was in the previous case manifested as energy of motion, is now transformed into thermal energy, and the sodium is heated and catches fire, giving a luminous flame and then an explosion. On striking a match the mechanical energy is transformed into thermal energy and the match is lit, transforming thermal and chemical energy into luminous energy.

We are, however, able to observe the most beautiful and marvellous examples of the transformations and indestructibility of energy every day in the case of the solar heat. This almost inexhaustible source of energy, which is given off by the sun without sensible diminution, is not lost. The heat which reaches the earth and is distributed over seas and continents, causing temperature disturbances at various points, also creates the aerial currents of the terrestrial atmosphere, and the energy thus formed is utilised in the sails

---

ether, diffused throughout the universe and penetrating all bodies and all space. (*See below:* Unity of Energy and Matter.)

Sound is transmitted by the vibrations of the air, and if an electric bell is placed under an evacuated receiver the sound no longer reaches our ear, whilst, on the contrary, the light of an electric lamp under the same evacuated receiver does reach our eye. The transmission of the light cannot be comprehended, except by the hypothesis of the cosmic ether. Previous to this hypothesis it was supposed that the propagation of heat was due to the detachment and expulsion of minute particles from the hot object, and that heat was in fact a sort of material, as was believed by Laplace (1749–1827); this notion caused great confusion in chemistry and physics, and retarded their progress. In 1758 Le Sage had ventured the hypothesis that heat was due to rapid vibrations of small particles of matter, as had previously been imagined by Bacon (1600). In 1799 B. Thomson (Count Rumford) considered heat to be a form of motion, and already ascertained with certainty that heat did not affect the weight of bodies. In 1800 Nicholson further defined the hypothesis of heat, attributing it to the vibration of the particles of matter which is the more intense and rapid the higher the temperature. The undulatory theory had already been upheld by Hooke (1650), Huyghens, and Euler (1707–1783) in order to explain luminous phenomena, but until 1800 the opposite theory of Newton, that is, the emanation theory, was generally endorsed. In 1810 Davy himself had accepted Rumford's theory of heat, but in the case of light he declared himself a follower of Newton's hypothesis of emission (1642–1727). In the meantime T. Young and Wollaston found themselves obliged to abandon the emission theory; but Fresnel was first able to show that the emission theory was erroneous by replacing it by his own very brilliant hypothesis, which more satisfactorily explained these important physical phenomena, namely, the hypothesis of a continuous elastic medium which penetrated all bodies and the entire universe. Poisson (1781–1840) gave concrete and rigorous form to this hypothesis, imagining the elastic medium to be composed of very small ethereal particles, vibrating intensely, by which means he was able to explain, and mathematically demonstrate, many physical phenomena which were otherwise inexplicable. Afterwards it was possible for Clausius (1857) mathematically to lay the foundation of his brilliant mechanical theory of heat. It is convenient to record here that to-day, after further study of electrical phenomena, the idea of an ether subdivided into minimal particles has been abandoned, that is, the theory of its discontinuity is now excluded; the study of cathode rays and of radio-activity has led to a species of return to the theory of material emanation, which has not yet found a clear explanation by the general laws accepted to-day.

of ships and of windmills. This beneficent heat also evaporates the water of seas, lakes, and rivers, transporting the particles of water vapour to greater altitudes and thus accumulating potential energy, which is again liberated when the vapour condenses to form rain or snow, and then descends in watercourses from higher to lower regions and the sea, returning the potential energy to nature in the form of mechanical, electrical, and thermal energy, moving the wheels of mills and turbines, which actuate dynamos giving motion, light, heat, and electricity in such a manner that the balance of nature is uninterruptedly maintained. This extends to all life, mineral, vegetable, and animal, in a marvellous harmony of simple and complicated transformations, to the nutrition of plants and animals, to human vitality, to thought and genius.

In the entire universe, whatever changes it is undergoing, has undergone, or will undergo in the future, there will always at each instant be found exactly the same unaltered sum of kinetic and potential energy. Helmholtz calculated that of the potential and mechanical energy which originally existed in our own solar system only the four hundred and fifty-fourth part still remains, the rest having been dispersed and transformed into heat, light, etc., during the passage from the nebulous stage to that of consistent nuclei; but none of this energy is lost to the universe (*see also* Radium).

However, it is not possible to suppose a complete inversion of the process of transformation of thermal into potential energy, because of the *degradation* which accompanies this change, that is, the impossibility of reconverting the entire thermal energy into kinetic energy on account of the fact that part of the heat remains inherent in matter.

In fact, if all the absolute heat of bodies were converted into motion one would arrive at matter deprived of heat and energy, which is unattainable and absurd because it is impossible to imagine matter without energy, as this would be equivalent to the disappearance of that matter. This explains the constant evolution which forces the entire universe continually to form itself anew; retrogression in nature is absurd; thus we are unavoidably impelled towards transformations ever more varied, but less convulsionary and more perfect, towards continuous and harmonic evolution (*cf.* Arrhenius, Das Werden des Welts).

We are able to apply with mathematical rigour this first law of thermodynamics or the equivalence of the various forms of energy, in order to demonstrate the practical impossibility of perpetual motion (*perpetuum mobile*). If we follow the cycle of changes produced in any material system by the displacement of energy (addition or subtraction of heat) in such a manner as to return to the starting conditions, we shall find that the work (A) produced by the system during the cycle will be proportional to the quantity of heat (W) imparted to the system, that is $A = J \,.\, W$, where J represents the factor of proportionality or the mechanical equivalent of heat (*see below*) and is independent of the nature of the system under consideration. With any change in the system the following changes of energy are connected: absorption or development of a certain quantity of heat, production of positive or negative work, and increase or diminution of the total amount of energy in the system. If dQ be the quantity of heat imparted, dU the portion of that heat which performs internal work and causes rise of temperature, and $J \,.\, dL$ that portion of the heat which is transformed into external work, dL, by increase of the volume or by overcoming pressure, then from the equivalence of heat and energy the mathematical expression of the first law of thermodynamics will be:

$$dQ = dU + J \,.\, dL$$

If U be the total quantity of energy contained in the original system, the system will be modified if we subtract a given quantity of energy, say, $U - U_1$, and we shall be able to return to the original system by restoring to the second system the exact quantity of energy ($U - U_1$) lost; if a lesser quantity of energy sufficed for this restoration, then by continuing this process in one sense or the other we should arrive at a creation of energy or perpetual motion.

The quantity of energy yielded up in the passage from the one state to the other is rigorously determined by the difference between the amounts of energy contained by the two systems; thus we cannot create energy without a corresponding amount of energy disappearing; the transformation of one form of energy into another occurs in each case according to a well-determined numerical relationship; and more especially in all cases a given amount of work is produced by means of heat, causing the latter to disappear, or, if work is transformed into heat, to appear.

This law of the conservation of energy was intuitively propounded in various branches of science in past centuries, by Galileo, Newton, Bernouilli, Rumford, and Davy, but was only enunciated in a precise manner by the Suabian medical man, Julius Robert Mayer, in 1842, whilst in 1847 Hermann v. Helmholtz, in his celebrated article on "The Conservation of Energy," discussed its general importance and applied it to all known phenomena; the rigorous, quantitative, and experimental demonstration was given by Joule in 1850, with his immortal researches on the mechanical equivalent of heat.

Not all the energy possessed by a system can be transformed, but only a part of it, called the free energy, which is utilisable, and to which the first law of thermodynamics refers; the energy of motion, external work, etc., of a system may be transformed into other forms of energy, for example, into heat, but the thermal energy cannot be completely retransformed into work. Later, in discussing the second law of thermodynamics, we shall study the limitations of the convertibility of one form of energy into another.

In the study of the transformations of energy, the law of the conservation of mass or of weight (or law of the conservation of, or indestructibility of, matter, as it was formerly less correctly called) is of special importance in chemistry.

Mass is one of the invariable properties of bodies, in virtue of which these bodies acquire a definite velocity under the influence of a definite quantity of kinetic energy. If two objects of the same nature but of different size, that is, containing different quantities of mass, move with the same velocity, they contain varying amounts of kinetic energy which are proportional to their masses, and, in general, the quantity of energy in a moving body is equal to the product of the mass and the square of the velocity. The mass of a body is simply its capacity for kinetic energy. A projectile with a mass of 8 kilos thrown with a velocity of 400 metres per minute produces the same effect (shock) on an impenetrable target as one four times smaller (2 kilos) with double the velocity (800 metres), since

$$8 \times 400^2 = 2 \times 800^2.$$

Mass is measured by taking as unit the mass of 1 c.c. of distilled water at a temperature of 4° and at 760 mm. pressure. But this unit of mass is also the unit of weight, as the mass of a body is proportional to its weight; it is called a *gram*. Various bodies which have the same weight acquire equal velocities under the impulse of equal amounts of energy, that is, they have also the same mass. And for this reason the two words are commonly used interchangeably, and for ordinary purposes mass and weight are equivalent words.

More precisely the weight of a body is simply the force with which it tends to approach the centre of the earth, and as the earth is not a perfect sphere, and its movement does not take place equally in every direction, the weight of a given body varies with the latitude and with the altitude, whilst its mass remains unaltered. This variation of weight occurs to an equal extent for all bodies placed under the same conditions, so that actually two different bodies which are equal in weight at any given point on the earth will still be of equal weight at any other point.

A century ago, before the classical researches of Lavoisier, who brought the balance into general use for the study of chemical phenomena, it was believed (and is still believed to-day by some ignorant people) that in certain cases matter is partially lost or consumed during its changes. A candle, a piece of wood or paper, etc., appear to diminish in weight continuously when burning, until nothing finally remains but a very little ash; it is hence supposed that the candle, wood, and paper are destroyed. In reality not only is the mass of these substances not destroyed during combustion, but if all the gaseous products of combustion are collected it is found that these weigh more than the combustible substance itself, because the materials of which the wood, candle, paper, etc., are composed have combined with the oxygen of the air, in the absence of which combustion does not occur. In fact, if we place on one pan of a balance a candle and a glass tube filled with caustic soda so arranged as to collect the products of combustion, then, on balancing these with weights in the other pan and lighting the candle, the pan containing the latter will gradually descend as the candle burns, demonstrating and confirming the increase of weight. An opposite impression to the apparent one produced by the burning candle is obtained by burning a very small amount of black gunpowder, which forms an enormous volume of smoke, giving the appearance of a real increase in the mass. On heating mercury thiocyanate (Pharaoh's serpents) a large increase of volume takes place which gives rise to the illusion of a large increase in the amount of material, but in reality it can be shown by means of the balance that the gain is only apparent. A minute turnip or beetroot seed buried in the earth reappears after some months in the form of a very large tuber, sometimes 500,000 times larger and heavier, some seeds weighing a few centigrams giving tubers weighing five or six kilos. But in this case also the weight and volume have been gained by the abstraction of various substances from the earth and the air.

Also among the more complex phenomena of physiology, all based on chemical and physical reactions, we meet again with the true indestructibility of mass. By weighing the materials excreted and food absorbed by any vegetable or plant whatever, we find that nothing is lost and that the part which is not assimilated is all found in the excretions of the organism. The vital phenomena of both animals and plants, from the most complex, such as those connected with human vitality, in which a man consumes about one-fiftieth of his weight in food daily, down to the most simple, such as those connected with the most elementary types of living beings, like amœbæ or certain micro-organisms composed of one cell or of a few cells, which are able to consume up to three hundred times their own weight of food per day with prodigious reproductive powers, a bacterium being able to generate thousands and millions of similar organisms in a few hours: all these vital phenomena are based on continuous chemical transformations, and these are always founded on the absolute indestructibility of matter.

In all the immense universe, in the infinite transformations which matter continually undergoes, not a single particle is lost, and the number of grams of matter in the universe is the same now as it was a million years ago and the same as it will be a million years hence.[1]

HISTORY OF CHEMISTRY

Now that we have sought to explain by rational hypotheses the essence of Nature in her various forms and transformations, we shall glance at past ages in order gradually to follow the investigations of our predecessors on this important question. We shall thus obtain an idea of the development of human thought in the interpretation of nature and of the principal phenomena which affect the human senses, and so arrive at an explanation of the manner in which the rational conceptions of modern chemical science arose.

THE EARLY CIVILISATIONS. We will turn backwards in the story of mankind, back to the commencement of historic documents and actual descriptions, and halt when the ancient legends no longer permit true history to become apparent. We will go beyond the Middle Ages, the Roman epoch, that of ancient Greece, 500 years B.C., and further back still to the first Egyptian civilisation. . . . But even then we must in fairness and justice pass beyond this to the ancient Chinese civilisation and the Assyrio-Babylonian civilisation, to a civilisation which is irrefutably recorded, and which would have been

---

[1] The law of the conservation of mass has not found any exceptions, and all the exact sciences accept as an undiscussed axiom the results of a century of varied researches and innumerable experiments. All the same, the experimental control of a law of such importance is always interesting, just as much so to-day, when science has at its disposal such perfect and rigorous apparatus, as in times past, from Lavoisier until now. Landolt and Heydweiller took up this question (1893, 1900, 1905) with the most exact experiments requiring a large amount of work. In two arms of a U-tube they placed two mutually reactive substances; the tube was then sealed in the blowpipe and the whole weighed on a most exact balance (weighing to 0·03 mgrm.); after agitating and mixing the two substances, and when the chemical reaction was completed, the whole apparatus was reweighed. Of seventy-five reactions, produced with hundreds of grams of materials, sixty-one showed a very slight diminution of weight, which in the case of silver sulphate and ferrous sulphate rose to 0·3 mgrm. per 100 grms. of silver. It has been argued from these facts that in the shock of the atoms producing the new chemical reaction minimal traces are split off from these atoms (they appear not to be electrons—*see* Electrons *below*) and are dispersed by passing through the walls of the glass vessel. As a matter of fact, on coating the walls of the reaction chamber with paraffin the diminution of weight disappeared, even in the case of ferrous sulphate and silver. In the last series of experiments carried out by Landolt until 1908 the small differences previously observed are explained; the small diminutions in weight are also obtained before the reaction if the substances are heated up to the temperature of reaction before they are mixed. With the help of a new balance sensitive to 0·006 mgrm., Manley continued Landolt's experiments up to 1912 and confirmed the earlier results.

still greater if, for their warlike and religious undertakings, the rulers had thought fit to demand conscientious and honest scientists.

Whilst in the rest of the world barbarism was still supreme, in China, 3000 years B.C. and in Assyria and Babylonia 5000 years B.C., there was already a civilisation much superior to that of the other nations, who were still groping in the primitive chaos of the rudimentary formation of human organisations. Agriculture flourished, and industry, which even many centuries later was in its infancy in other continents, had risen to important development in these parts of Asia.

We stand astonished before the art of our greatest artists, before the pictures of the period of Giotto and the Byzantine epoch; but what shall we say of the truly admirable works of art which the yellow man produced 2000 and 3000 years previously?

When we admire the very beautiful works of Michelangelo, who reproduced nature so ably and studied plastic anatomy by dissecting parts of animals and plants in order to examine them more closely, what shall we say of the surprising reproductions in pictures, sculptures, and carvings made by Chinese about 2000 years earlier and by the most ancient Egyptians 4000 years before?

Faithful and marvellously exact reproductions of nature alive and dead on linen, bronze, copper, stone, and silk, and with such harmonious and simple artistic feeling that they are capable of inspiring the artists of to-day! Even 1000 years prior to the Christian era the walls of the Chinese palaces were painted and decorated; and 2000 years B.C. the art of portrait painting flourished.

Whilst the powerful Romans in their frenzied luxury, which led to corruption of their morals and total decadence, used rich silken fabrics imported from Asia, in China the manipulation of silk was already well understood 2200 years B.C. under the Ju dynasty, and was in fact rapidly approaching perfection. Only 150 years B.C. the daughter of a Chinese emperor introduced silk manufacture into Japan, and from there it slowly extended throughout Asia; only in the third century of our era was it imported into Italy, and the culture of the silkworm commenced in that country only in the year 600.[1]

The manufacture of paper in Europe dates from about A.D. 1200, whilst in China paper made from hemp and bamboo fibre was known as early as 360 B.C., and in 105 B.C. a Chinese, Tsai-lun, taught the manufacture of paper from silk and linen rags.

Gunpowder, which was first used in Europe about A.D. 1200, was prepared in various ways in China many years before the Christian era, and was introduced into Europe by the Arabs.

The Chinese were real adepts in the smelting of minerals and of bronze 1800 years B.C. In the Imperial Museum in Pekin there are collected the historic treasures of the Chang dynasty (1766 B.C.) which testify to the delicacy and perfection of the sculpture and carving, which are equal, if not superior, to the best art of Greece and Tuscany; our modern Western civilisation, in its comparatively recent vandalic invasion of the City of Heaven, might at least have refrained from laying its hands on these artistic and historic treasures.

The working of wood and leather and the preparation of varnishes are also extremely old in China. The production of porcelain, which dates from the eighteenth century in Europe, was already known in China ten centuries previously.

But the Chinese have precedence not only in ancient, but also in comparatively modern, chemistry. We revere Priestley, who discovered and isolated the important element oxygen in 1774, and we admire the work of the celebrated Lavoisier and of Cavendish in connection with the composition of water in or about the year 1783, but it has now been shown by Duckworth (*Chem. News*, 1887, LIII, p. 250) that the Chinese knew of oxygen and the composition of water much earlier than Priestley and Lavoisier.

The Chinese were very well aware of the hygienic and domestic importance of water, and were the first, already in very remote historic times, to drill numerous wells of the kind now known as artesian in order to obtain good water from the subsoil, whilst even to-day many Italian towns and country places are without potable water.

---

[1] The Chinese were well acquainted with the dyeing of fabrics. The use of indigo also originated with the old Chinese civilisation, as the indigo-blue fabrics found in Europe, even at the time of the decadence of Rome, all came from the East; this was proved by an analysis of the remains of the mantle of St. Ambrose by Prof. Frapoli (1872) and by Prof. Carnelutti (1884) at the Society for the Encouragement of Arts and Manufactures of Milan.

Even in their philosophic disquisitions on the essence of nature and of the universe we find amongst this people ideas and conceptions inspired by very pure justice and morals—conceptions much clearer than those of the Greek philosophers who lived several centuries later. When Confucius, the founder of the philosophic religion of China (550 B.C.), conceived the essence of nature to be "matter inseparably united to a virtue of matter itself, and to the continuous interchange of matter and of this virtue," he had realised the origin, essence, and rule of life.

EGYPTIAN CIVILISATION. After that of the Chinese the oldest civilisation is the Egyptian, especially in reference to the origin of chemistry and to the large number of experimental observations made and ingeniously utilised in order to increase the comforts of life. During the last ten years important discoveries have been made on the ancient Egyptian civilisation which show that even 4000 years B.C. it had in many points almost excelled the civilisation of China.

If we turn to the works of art of this period (even 2000 B.C.) we find that the Egyptians knew how to prepare various metals and alloys; they were well acquainted with dyeing, glass manufacture, and also the preparation and employment of pharmaceutical products and antiseptics.

Chemistry was considered a sacred art; it was exercised by priests and was accessible only to the elect. The temples were connected with laboratories in which chemical operations of every kind were conducted.

Even the origin of the name "chemistry," now so much discussed and debated, must almost certainly be sought in the name Chemia, which the Egyptians gave to their country, on account of the black colour of the soil (they called the pupil of the eye by the same name). Therefore the first ideas of chemistry in Europe came from Egypt, imported by the Greeks and Romans, and later by the Arabs, so that it is probable that by "chemistry" they understood the science and art of the country of the Egyptians (Chemia).[1]

The Egyptians were fully aware of the putrefactive action of the air on corpses, and, therefore, preserved their dead out of contact with the air. Everybody knows how the Egyptian mummies have been preserved unaltered down to our own times.

The Egyptians were the first to construct wells lined with masonry in order to obtain good and wholesome water, whilst the other early peoples made use of the water of springs or tanks (except the Chinese, who already used artesian wells).

All the objects of art of the early Egyptians (statues, ornaments, temples, etc.) in wood or stone, were painted in various colours. Paintings produced 1600 B.C. show distinctly the use of fifteen different colours. White paint was prepared from gypsum mixed with white of egg or honey; yellow was obtained with natural arsenic sulphide or ochre, red with ochre or cinnabar, blue with lapis lazuli (an aqueous phosphate of aluminium, magnesium, and ferrous iron) or with powdered copper sulphate, black with animal charcoal; a little gum tragacanth was added to the water used in mixing these colours.

The art of design in Egypt dates from prehistoric times. It became bizarre because it did not consider the perspective of the human body. It is found that in design, as a general rule the legs and feet are drawn from the side, the bust from the front, the head in profile, and the eye from the front. The manufacture of glass vessels among the ancient Egyptians was very noteworthy. They also knew and made use of soda, potash, alum, nitre, iron, copper, tin, lead, gold, and silver.

The scientific activity of the Egyptians was concentrated in Alexandria, which was the most important city in the world apart from Rome. In Alexandria the best scientific and philosophical institutions existed together with the world's largest library, containing 700,000 volumes; but this was completely destroyed in the year 641 after the Arab invasion.

INDIAN AND GREEK CIVILISATION. The Egyptian civilisation was closely connected with that of the Greeks, who obtained much of their knowledge of nature and

---

[1] The word "chimica" was already used in writing in the time of Constantine the Great (A.D. 325) in a book of Julius Firmicus Maternus, a writer of that epoch, in which, dealing with astronomy, he declares that the position of the moon, relatively to a given planet, influences the fate of those born at the time, and thus when the moon is near Saturn those born at that time are destined to study "chemistry." But it can be safely maintained that the word chemistry was well known to the Emperor Diocletian (A.D. 300), who stated with pride that he had caused to be burnt all the Egyptian books which spoke of the chemistry of gold and silver.

philosophy from Egypt. We will only refer to those matters related to the history of chemistry.

For the sake of historic accuracy it is, however, well to remark that the fundamental conceptions on the nature of the universe, attributed by almost all historians to the first Greek philosophers, have their real origin in India. The Indian civilisation was in some of its manifestations, especially in the realm of art, superior to that of Egypt. It is maintained in various Indian writings that the whole world is composed of four elements, water, earth, wind, and fire, and that everything is produced by their union; to these the philosophy of the sect of the Djainas added a fifth element, the ether, whilst Buddha (623–543 B.C.) introduced a sixth, namely, consciousness; the Buddhists believed in Nirvana, that is, the end of all beings and return to nullity, to universal emptiness, to unformed nature, and, forestalling Schopenhauer and many modern positivists, they confusedly denied the existence of matter, maintaining that everything which exists is nothing more than a collection of subjective impressions.

In the Greek civilisation we find, 600 years B.C., Thales, one of the seven wise men of Greece and a contemporary of Solon, who considered the whole of the universe to be derived from one single substance, water. Very soon afterwards (550 B.C.) we have Anaximenes, who considered air to be the primary material, with the property of infinite movement; Heraclitus (500 B.C.) maintained and pretended to demonstrate that the essence and origin of nature and of matter was *fire*. Anaxagoras (500 B.C.), on the contrary, believed that nature was formed from a single, continuous, and uninterrupted material, infinitely divisible without any interspace (the hypothesis of *homeomeria*), and not endowed with a movement of its own, but with movements imparted to it by an immaterial, supernatural intelligence.

All these are vague rudimentary conceptions of the unity of matter to which, after many centuries, we try to return to-day, supported by the latest deductions of positive science.

About the year 430 B.C. a more brilliant philosopher, Leucippus (born at Elea), disheartened by the "numbers" and obscure philosophy of Pythagoras and the sophisms of his master Zeno, devoted himself to the study of nature. By abandoning all preconceived ideas, he came to the conclusion that the universe is infinite and that the filled, ponderable part of it is composed of extremely small particles or imperceptible atoms of determinate form varying from substance to substance; these infinitely numerous atoms move in empty space, collide with one another and occasionally unite with similar atoms.

We have here the real origin of the atomic theory, the foundation of modern chemistry, which remained buried for about twenty-four centuries.

After the death of Leucippus he was followed by Democritus (born about 400 B.C.), who is so well remembered in connection with the history of philosophy. He continued to teach the opinions of his master on the essential character of nature, adding that all the atoms are composed of a single substance, differing only in their form, by means of which they give rise to the various bodies and to their properties. He taught also that the atoms are endowed with continuous motion, and that matter is eternal.

The only followers of Democritus were Epicurus, 350 B.C., and Lucretius, 90 B.C. It seems incomprehensible to-day that such a brilliant hypothesis should have been disregarded for so many centuries, as it contributed so largely later to the formation of modern chemical theory.

A philosopher of Sicilian origin (from Agrigentum), but who had lived for long in Greece, named Empedocles (490–430 B.C.), united to a brilliant intelligence the most impudent quackery, arrogating to himself almost Divine qualities. He believed in the atomistic theory in order to explain the intimate nature of matter, but maintained on the other hand that matter manifests itself to us through four fundamental elements, namely, water, air (the "wind" of the East Indians), fire, and earth. This subdivision, which lasted through many centuries, is certainly much less brilliant than the theories of Leucippus and Democritus, and was evidently taken from the Indian philosophers.

Then comes Aristotle (384–322 B.C.)—a pupil of Plato—to whom many historians erroneously attribute the theory of Empedocles on the four elements. Whilst Aristotle had undoubtedly brilliant conceptions in abstract philosophy, since he dared to affirm for the first time that the human mind is like a blank tablet on which experience writes that which is perceived by the senses, in the observation of natural phenomena he increased the confusion due to Empedocles, and starting from the manifestations of the four elements, he deduced four essences of nature, namely, heat, cold, humidity, and dryness. According to him, water was composed of cold and humidity; earth of cold and dryness; air of heat and humidity; and fire of heat and dryness. As these four elements were insufficient to explain all natural phenomena, he imagined a fifth of a superior order, which he called the fifth essence (*quinta essenza*), which was, however, of an ethereal character, more or less spiritual and diffused through the universe. Here also we find an adaptation from the Indian philosophy. We owe to Aristotle the first attempts to apply the experimental method in science. Wishing to discover whether air possessed weight, he placed an inflated bladder on the balance and then deflated it. As he found no difference in weight after deflation he concluded that air had no weight. Continuing his studies on the nature of air he was led to deny the possibility of a vacuum, and the aphorism "Nature abhors a vacuum" is due to Aristotle. This idea was maintained for many centuries until the time of Galileo.

In the time of the Greeks six metals: gold, silver, copper, iron, lead, and tin, were already well known, as were also the methods of treatment of various ores. Dioscorides (A.D. 50) prepared mercury from cinnabar.

ROMAN CIVILISATION. The evolution of experimental methods as applied to science received a great impulse from Archimedes (280 B.C.), who by measuring specific gravity was able to determine how much silver was contained in the crown of King Hiero.

Roman civilisation had little influence on the progress of chemical knowledge and the study of nature. Civil legislation, art, and the desire for conquest and warlike rapine did not leave much time for such studies, but we may recall the marvellous and colossal hydraulic works of the Romans which furnished Rome with abundant supplies of good water. Rome had fifteen aqueducts, and the three which remain to-day alone suffice to supply water to the whole of the city. From this one sees that water was then used abundantly for baths and other purposes.

We must also note Pliny, who was born at Como A.D. 23, and who died in the year 79 in the neighbourhood of Vesuvius during the famous eruption which buried Pompeii. He collected, in a species of encyclopædia of thirty-seven volumes, the "Historia Naturalis," which has survived to our times, all the natural knowledge which existed at his epoch. This work, often confused and contradictory, contains many unconfirmed statements which were collected purely for purposes of reference and form a valuable record of the chemical knowledge of the period.

At the time of Pliny chemical theory was still based on the four Aristotelian properties of matter, and Pliny himself stated in all sincerity and certainty that rock crystal was nothing else than powerfully frozen water, frozen much more than ice. According to Pliny cold had the natural property of solidifying and hardening. Pliny indicates in his "Historia Naturalis" that air is changed into water, with formation of clouds, and that these are again transformed into air by evaporation.

For many centuries afterwards chemistry remained under the domination of the Aristotelian conceptions. These conceptions on the transformations of matter gave rise to the belief in the possible transformation of other metals into the noble metals, so that the chemistry of the Middle Ages became a sort of magical speculation, and was limited to attempts to manufacture gold from other metals.

ARAB CIVILISATION. Egypt gave a strong impulse to the development of chemistry and of philosophy. It was from Egypt that chemical science was rapidly diffused by means of the Arabs. The Arabs invaded Egypt in 640 and conquered the whole of Northern Africa and finally even Spain. They continued the attempts to manufacture gold and silver. The word *chimica*, which they found in Egypt, was by them modified by adding the Arab definite article, and they thus formed the word "alchimia" (alchemy).

The greatest and most famous Arab alchemist was Gebir, whose fame was universal and whose writings were generally consulted and afterwards translated into Latin. He lived about A.D. 800, and being a follower of the principles of Aristotle, he undertook a series of chemical experiments in order to effect the preparation of gold. He also described in detail furnaces, retorts, and much other apparatus. He succeeded in purifying many substances by means of solution, crystallisation, filtration, distillation, and sublimation. He was acquainted with alum, green iron vitriol, saltpetre and sal ammoniac. He describes for the first time nitric acid and aqua regia; he prepared many derivatives of mercury, and it is not impossible that he already knew of sulphuric acid.

Starting from the Grecian philosophy and whilst investigating the possibility of preparing gold from other metals, Gebir propounded a new chemical theory, according to which all the metals always contained two substances in variable proportions according to their nature. He believed these two substances to be mercury and sulphur. The former produces fusibility, ductility, and metallic lustre; sulphur, on the other hand, produces the various modifications which the metals undergo when heated. By varying the proportions of these two elements, we should be able to pass from one metal to another. Gold and silver, according to Gebir, contain much mercury, and are, therefore, very lustrous; gold, however, also contains yellow sulphur, whilst silver contains white sulphur.

This phase of chemistry, called alchemy, lasted until the thirteenth century under the influence of the Arabs, and then extended rapidly from Spain throughout Europe; thus we find Lull in Spain in 1200; Villanova in France in 1300; Magnus in Germany in 1250, and Thomas of Aquinas (the saint) in Italy in 1250—for he also was an alchemist and studied many minerals.

The alchemists of this period are represented with long hair and a beard, as persons clothed in ample vestments and locked up in impenetrable laboratories, completely intent and absorbed in the search for gold. Later, Basil Valentine (a German monk of whom the true family name is not known) dedicated himself about the year 1500 to the search for the philosopher's stone, by means of which all metals and other objects would be converted on contact into precious metals. It was believed, further, that it would be possible by means of the philosopher's stone to restore youth to the aged.

Certain facts supported these alchemists in their pretensions to manufacture gold from other metals. These consisted in the fact that during prolonged treatment of certain ores traces of gold resulted. It is no longer doubted that this gold is simply present as an impurity in the ores employed.

An alchemist of Hamburg named Brandt searched for the philosopher's stone in urine in 1669. He heated and slowly evaporated enormous quantities of urine in large alembics, hoping finally to discover the famous stone. As it happened, to his extreme surprise and the intense amazement of his contemporaries, he actually obtained a new substance which evolved light in the dark, namely, phosphorus.

To the two components of metals, mercury and sulphur, Basil Valentine added a third, namely, salt, the study of the metallic salts commencing at that time.

IATROCHEMISTRY. With Paracelsus, a Swiss (1493–1541), a new phase of alchemy commences, called iatrochemistry, that is, the chemistry of medicines to prolong the life of mankind. Paracelsus combated the theories of the celebrated medical men Galen (A.D. 131) and Avicenna, an Arab (A.D. 800). He considered man as a chemical combination, and stated that illnesses occurred because this combination was altered; consequently illness could be cured only by chemical means. The purpose of chemistry, according to him, was not to search for gold but to prepare medicines, and this search led him to important discoveries. He travelled throughout Europe, Egypt, and Turkey, was Professor of Medicine at Basle, and died at Salzburg in very great poverty. This was the bitter reward for his honesty, as he always fought against the quackery and stupidity of the self-styled manufacturers of gold, by whom he was persecuted, directly or indirectly, until his death. The contemporaries and successors of Paracelsus were Agricola in Germany (1490–1553), who carefully studied the smelting of metals, and Libavius, also in Germany (1540–1616), who wrote the first text-book of alchemy, in which he collected all the chemical knowledge of the time; Van Helmont of Brussels (1577–1644), who was a medical man of world-wide celebrity, studied alchemy in the same sense as Paracelsus, distinguished for the first time various kinds of gases, and identified the gas produced in fermentation with that from the Grotto of Dogs (near Naples).

He believed vaguely that the first cause of all things was water and something supernatural which was combined with it.[1]

---

[1] To form an idea of the extravagant conceptions held even by the Iatrochemists with regard to medicines and the cause of diseases, it is necessary to read the writings of Van Helmont (1626) on "The Causes and Nature of Fever." We will confine ourselves here to translating the recipe of his celebrated ointment which was supposed to cure any fever, especially quartan-fever: "One heats in a brass pan $1\frac{1}{2}$ oz. of turpentine of Cyprus and then introduces fifteen live spiders and mixes until the spiders have disappeared; one then places the whole on the fire and continues to stir, introducing as many cobwebs as the spiders would presumably have spun, or, if cobwebs are lacking, one adds nine other small spiders and agitates further; one

The first to attack openly the Aristotelian hypothesis on the constituents of nature, heat, cold, humidity, and dryness, were: the brilliant but not always sincere English philosopher, Francis Bacon (1561–1626), who revived the atomic hypothesis of Democritus, maintained that matter was indestructible, and intuitively guessed by means of philosophical speculation the existence of universal gravitation; he clarified ideas on the inductive method applied to science, basing natural laws on known facts and on experience, in a manner first started by Palissy, Leonardo da Vinci, and Paracelsus. He may be considered as the first founder of the inductive method (*see below*).

Bacon defined heat as the effect of a motion, extension, and undulation of the smallest particles of substances. Then Glauber (1660) cleared up the composition of salts, especially of sodium sulphate, which still bears his name (Glauber's salt), and initiated the development of technical chemistry, although he always remained a follower of iatrochemistry.

Lemery (Rouen, 1645–1717) extended the conceptions of chemistry, and in his "Cours de Chimie," published in 1675, divided this science into the study of organic substances (animals and vegetables) and of inorganic substances (minerals). In a few years thirteen editions of the book were published. Before this time the greatest confusion reigned in the classification of substances. It will suffice if we cite a single example. Antimonious chloride was called butter of antimony on account of its white, pasty appearance, and for this reason was classed side by side with ordinary butter from milk.

PNEUMATIC CHEMISTRY. Whilst alchemy and iatrochemistry were gradually losing ground, Robert Boyle (1627–1691) founded a new era in chemistry, namely, that of pneumatic chemistry, which was concerned specially with the study of gases. He defined more exactly the nature of elementary bodies and of chemical compounds, and showed that chemistry should not serve mainly for alchemistic or therapeutic purposes, but should form a study apart, constituting one of the natural sciences.

Boyle was the first in England (at the University of Oxford) to erect a chemical laboratory for experimental research, and was supported in this by all the other professors. He obtained nitric acid by distilling nitre with sulphuric acid; he discovered the characteristic reaction of copper with ammonia, of chlorides with silver nitrate, and of iron with tannic acid; he perfected the air-pump, and studied combustion in a vacuum; he found that sulphur will not burn in a vacuum, and that the flames of hydrogen and of a candle die out, whereas gunpowder ignites in a vacuum if heated on an iron plate, and fulminate of gold explodes in a vacuum under the influence of light rays concentrated by means of a lens. He thus deduced that the substance which supports combustion in air is analogous to that contained in the nitre which forms one constituent of the gunpowder.

Boyle was the first to state that on burning or heating metals in a furnace, these show an increase in weight after cooling; thus on heating mercury another substance is formed because the mercury absorbs or combines with some part of the products composing the flame.

---

then adds 1½ oz. of good asphalte and 1 oz. of white sal ammoniac, and allows to cool until one obtains a paste which is allowed to stand for fifteen days. Meanwhile one prepares a special oil in the following manner: One mixes oil of fresh water-lily flowers, one year old, with oil of bitter almonds; nine live scorpions are then introduced and the whole is exposed to the sun when this is in the constellation of the Virgin or of the Crab, and it is left thus until the scorpions are dead; 1 oz. of pastel of female vipers is then added and it is left in the sun for a further fifteen days. The oil is then ready. The paste is then softened on the fire, and worked up by means of the hands with the prepared oil in such a manner that a paste is obtained, this being spread out on a skin, which is then cut into pieces as large as a dollar. And now follows the method of application: An hour before the fever appears one ties two of these ointment preparations to the wrists of the patient and leaves them for exactly nine days (nine were the small spiders and nine the scorpions !), takes them off at the same hour at which they were applied and throws them into running water. Whatever be the nature of the fever, after this cure it will disappear."

Who would suppose that after four centuries, even in Italy amongst the ignorant mass of the cities, similar recipes are still largely used? Still more remarkable are the ideas of Paracelsus. His sudorific with a mercury base was celebrated for a long time, and was supposed to cure an extraordinary number of maladies.

In 1894 two interesting documents, which show that alchemy survives even in our own time, were brought to light (*Chem. Zeitg.*, 18, p. 1998). These are two letters of a modern German alchemist who offers himself to the owner of a copper mine to place at his disposal his secret for extracting £12 worth of gold from each 50 kilos of old copper, whatever may be its origin, and demands a fee of 10,000 thaler (about £1600) for revealing the said secret, which had cost him thirty years of work.

CHEMISTRY OF PHLOGISTON. The study of combustion occupied the chemists of this epoch for another century, commencing with Hooke (1635, the inventor of the pocket-watch) and Mayow (1645)—both pupils of Boyle—who demonstrated that the gas formed on heating nitre is the same as that which is found in air and which maintains the combustion of a fire and the vitality of animals. Mayow showed that there is also a gas in air which does not maintain combustion. Becher (1635–1682) brought forward a new hypothesis on combustion, which was defined and developed by Stahl (1660–1734), and regards all combustible bodies as formed of at least two components, one of which is evolved during combustion, the other remaining. On calcining a metal in a furnace one of the components, called phlogiston, escapes, and the calx of the metal, which we to-day call the oxide, remains. Thus a metal is composed of phlogiston and of the calx of the metal (oxide). On heating a metallic calx with carbon the metal is re-formed, that is, the carbon has restored phlogiston to the calx, forming the metal. As a result of this theory it followed that the metals were compound bodies, the weight of which should diminish on heating, because they lose one of their components, the phlogiston. But in practice this is found not to be true, for metals increase when heated in the air, as Boyle had already observed. The supporters of the phlogiston theory explained this evident contradiction of their hypothesis by supposing that the increase of weight was due to the increase of density (according to which reasoning compression of a bundle of straw would increase its absolute weight).

The phlogiston hypothesis, however erroneous, contributed very much indirectly to the development of chemistry, because by generalising and applying it to numerous substances, discoveries of new bodies and studies of very varying phenomena were made.

Various gases formed during combustion were studied and knowledge of the behaviour of metals in general was increased.

The first formidable attack on the phlogiston hypothesis was made by Black (1728–1799), who showed in 1755 that on heating magnesia alba to redness a constant quantity of fixed air (carbon dioxide), and not of phlogiston, was evolved, and that the weight of the remaining magnesia was less.[1]

Black may thus be considered to be the founder of quantitative gravimetric chemistry, although the control of chemical phenomena by taking the weight into account had already in some cases been exercised by Boyle. Black discovered carbon dioxide, which he called "fixed air," and identified it in many varied cases: on heating magnesia to redness or treating it with acids, on burning carbon, on breathing, etc. He also discovered the specific heat and latent heat of bodies.

Pneumatic chemistry, which had its origin in the experiments of Van Helmont (1640), who was already vaguely acquainted with carbon dioxide and other gases, and which was developed by the work of Boyle, Hooke, and Mayow, was greatly extended by the work of Black.

But the greatest contribution was due to Priestley (1733–1804), who also studied the gases of combustion, and those resulting from the respiration of animals and plants. He discovered nitrogen, carbon monoxide, nitric and nitrous oxides, and the still more important gas, oxygen, by heating mercuric oxide (August 1, 1774) in a vacuum with the help of a strong lens, and was the first to determine with exactness the specific gravity of gases. He always remained a faithful and tenacious supporter of the phlogiston theory.

Cavendish (1731–1810) was a more exact experimentalist than Priestley. He discovered hydrogen by treating metals with dilute acids (1766). He showed that by combustion of hydrogen, water alone was formed (1781, together with Watt). He also discovered that air is a simple mixture of two gases, oxygen and nitrogen, which are mixed in well-defined and constant proportions.

Contemporaneously, but independently, the Swede, Scheele (1742–1786), also arrived by other means at several discoveries, and apart from oxygen, he discovered nitrogen, chlorine, many organic and inorganic acids, glycerine, etc.

The history of the period of the older chemistry now ceases, because with Lavoisier, that is, with the end of the eighteenth century, we commence the

---

[1] We can to-day justify the phlogiston theory if for the word "phlogiston" we substitute the word "energy" (heat); we would then understand that on heating a metal which oxidises there has been a loss or development, not of phlogiston, but of energy.

history of modern chemistry, which has been the carrier of such abundant benefits to progress and civilisation, surpassing in a single century all which had been produced during the previous forty centuries. Boyle had already stated that chemistry should be considered as a science apart, as a distinct branch of the natural sciences. Stahl had defined chemistry as the science which has for its scope the resolution of compound substances into their constituent elements and the reconstruction from them of other substances.

Summarising the state of chemical theory and knowledge towards the middle of the eighteenth century, we find that seventeen elements were known at that time and that the metals were subdivided into: Perfect metals, such as gold and silver; imperfect metals, such as copper, iron, tin, lead, and mercury (because this latter could be frozen!); semi-metals (*i. e.*, those which were less ductile), such as arsenic, antimony, bismuth, zinc (discovered in 1735), cobalt (in 1751), nickel (in 1774), manganese (about 1780), molybdenum and tungsten; platinum (1750) was considered as a special metal. The different metals were still considered to be combinations of phlogiston with the calces of the metals. Sulphur, phosphorus, and carbon were regarded as combinations of phlogiston with the acids corresponding with these substances. The alkalies, the alkaline earths, and the earths themselves (alumina, silica, etc.) were considered to be allied to the metallic calces. It was known that metals reacted with acids. The simple gases which were known were inflammable air (hydrogen), also called pure phlogiston, oxygen, nitrogen, and chlorine.

About the year 1772 Lavoisier devoted himself to the study of combustion, and came to the conclusion that the phlogiston theory of Stahl was completely erroneous and did not correspond with the facts. He showed by means of the balance that when sulphur or phosphorus is burnt there is no loss, but on the contrary an increase, in weight, due to the union of the sulphur or phosphorus vapours with the air.

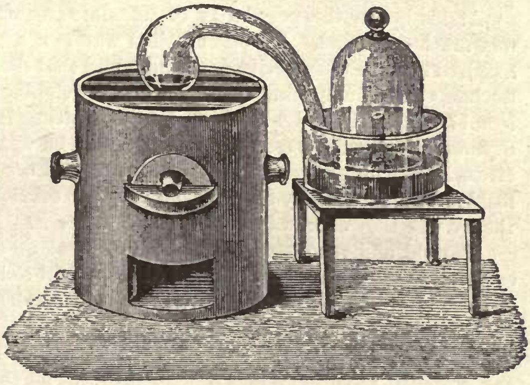


FIG. 1.

In 1773 Lavoisier investigated the character of the air (or gas) evolved in respiration, combustion, and fermentation.

In 1774 he found that on heating tin and lead in a closed flask no increase in weight occurred, whilst when the flask was open the weight increased through combination with a portion of the air in the flask, and that the air which remained was different from the ordinary air and from the air which was fixed by, and combined with, these metals.

In 1778 he found that on heating red mercuric oxide a very active gas is evolved which intensifies combustion and is concerned in the calcination of metals. He at first called this gas *pure air* (Condorcet called it *vital* air), but at a later date he named it *oxygen* (*i. e.*, generator of acids).

The discovery of oxygen is ordinarily attributed to Lavoisier, but it has now been shown that Priestley had already prepared it by the same method and had studied its properties (August 1, 1774), and that Scheele knew this gas at a still earlier date, namely, in 1771.

The composition of air was not clearly known at this time, but Lavoisier showed that on heating mercury for eleven days in a retort connected with a bell-jar filled with air the volume of the latter is diminished and the weight of the mercury increases, whilst the gas which remains is incapable of supporting life (Fig. 1). This gas was nothing else than nitrogen, and in this manner air was shown to be a mixture of oxygen and nitrogen.

In 1781 Lavoisier discovered the composition of water, showing that it was formed by the combination of oxygen with inflammable air (hydrogen), and in the years 1781 to 1783 he decomposed water in various ways into its components, hydrogen and oxygen (action of steam on red-hot iron, etc.).

The composition of water, which had been considered to be a simple substance until that time, was thus clearly elucidated. But we now know that in 1781 Cavendish had already showed experimentally, shortly before Lavoisier's experiments, that water is formed by burning hydrogen, owing to the combination of this gas with atmospheric oxygen.

We may consider Lavoisier to be the founder of more definite quantitative analysis, and to him has been attributed the introduction of the balance as applied to the study of chemical phenomena. But Boyle had already found that mercury increases in weight on heating; and the gravimetric experiments of Black in 1755 show that the balance was then already used in the study of chemistry.

The true merit of Lavoisier lies in his generalisation of the use of the balance in the study of chemical phenomena and his experimental demonstration of the indestructibility of matter: nothing is created and nothing destroyed in the universe.

At his epoch the possibility of transforming water into earths by prolonged boiling was much discussed. Lavoisier boiled water in a weighed and closed glass flask for one hundred and one consecutive days and found that the weight of flask with contents remained unchanged; on emptying the water and reweighing the empty flask he found that it had lost 17·4 grms. in weight, whilst on evaporating the water originally contained in it to dryness he obtained a residue of 20·4 grms.; he was thus able to demonstrate (apart from errors in weighing) that the water had dissolved a portion of the glass. Indeed, when the residue was analysed by Scheele he found it to consist of silica and alkali. The Aristotelian theory was thus definitely buried for all time.

The old and renowned chemists of Lavoisier's epoch did not accept the new theories, especially that of combustion, and died faithful followers and supporters of the phlogiston theory, although this had been inexorably condemned by the numerous and rigorous experiments of Lavoisier.

On the other hand, the whole newer generation of European chemists at once embraced and accepted Lavoisier's theory with enthusiasm, and from that time chemistry developed in a marvellous manner, which has never been equalled in the history of any other science.[1]

[1] *Biographical note.*—Lavoisier (Antoine Laurent) was born in Paris on August 26, 1743. His family was rich, his father being an advocate, and Lavoisier studied mathematics, physics, astronomy, mineralogy, and botany at the Mazarin College; with this vast scientific patrimony he turned, whilst still a youth, to the study of chemistry, in which he accomplished a real revolution and initiated a new era which is still animated to-day by the effects of his brilliant discoveries.

In spite of his great services it is impossible to overlook the sins of Lavoisier in appropriating to himself discoveries made by chemists who were his contemporaries or predecessors. Oxygen was first discovered by Hales in 1727, and had already been prepared from mercuric oxide by Priestley in 1774, by Bayen in the same year, and still earlier by Scheele in 1771. It was at a dinner at Lavoisier's house that Priestley confidentially communicated his discovery to Lavoisier, in 1774; in 1778 Lavoisier then claimed the discovery for himself, whereas in reality he had merely given the name of oxygen to the new gas.

In a similar manner Lavoisier claimed for himself the discovery of the composition of water, whilst, as is now known, Blagden, a friend of Cavendish, when visiting Paris in 1781, told Lavoisier that Cavendish had discovered the composition of water in a very simple manner by burning inflammable air (hydrogen), as water alone was formed during this combustion.

Lavoisier and Laplace immediately repeated the experiment and then communicated the discovery to the French Academy in 1783.

These facts certainly do not obscure the fame of the great scientist when we remember his eminent services, but in the interests of historic accuracy and justice it is impossible to pass them over in silence.

In December 1793, before the end of the revolutionary Reign of Terror, Lavoisier was accused of conspiracy against the new Government and fraud against the people by preparing snuff containing much water and noxious substances, was arrested, together with twenty-seven other *fermiers généraux*, and condemned to death. It was in vain that he asked for a few weeks of liberty in order to conclude certain important experiments on respiration which would benefit the whole of humanity. This was denied to him, and Lavoisier was beheaded on May 8, 1794.

The severity of the Revolutionary tribunal was due to the profound and intense hatred

THE FUNDAMENTAL LAWS OF MODERN CHEMISTRY

About 1650 Glauber made an important observation, which was of much consequence later when chemistry had disentangled itself from the fetters of alchemy. He was trying to discover how the decomposition of certain salts by means of acids occurred, and he observed that when two neutral salts react upon one another their components are reciprocally interchanged, giving rise to two new salts, saturated and neutral like the first (mercury chloride with antimony sulphide).

In 1700 Homberg also made an important experiment on the various quantities of basic (alkaline) substances which are needed to saturate a certain constant quantity of a given acid.

The first positive law arose from the immortal work of Lavoisier, who, by the universal and rigorous use of the balance in the study of chemical phenomena, showed that "the sum of the weights of two substances which combine is equal to the sum of the weights of the new combinations which are formed"; thus, for instance, on combining 8 grms. of oxygen with 1 grm. of hydrogen, the quantity of water which is formed is exactly 9 grms. "Nothing is lost and nothing is created," said Lavoisier, thus stating a most important law of nature, that of the conservation of matter.

On the other hand, Wenzel in 1777 published his important "Study on the Affinities of Substances," in which, based on an enormous number of analyses, carried out with great exactness, he demonstrated that acid and basic substances combine with one another in constant quantities, then confirming and amplifying his studies by means of reactions which occurred between neutral salts.[1]

---

amongst the people towards the *fermiers généraux,* who imposed an excessive taxation, ruthlessly aggravating the already miserable condition of those who contributed to support the weight of the triple domination of State, nobles, and clergy. The population of France, of 26,000,000 inhabitants, had to provide £19,000,000 a year towards the revenue of the king, and had to submit to vexatious taxation on the part of 140,000 nobles and of 130,000 clergy.

The *fermiers généraux* were entrusted with the collection of the most odious of these taxes, the monopoly of tobacco, the tax on beverages, and more especially the tax on salt. Each year 300 contrabandists were condemned to hard labour.

Renauldon, at the beginning of the revolution, wrote as follows: "The *fermier général* is a rapacious wolf, who impoverishes the earth, draws the last halfpenny from it, oppresses the labourers, reduces them to beggary, lays waste the fields, and renders odious the master who is obliged to submit to this taxation."

It is said that Lavoisier accumulated £48,000 in profits in a few years from his office as *fermier général.* This was fatal to him.

His chemical friends—and he had influential ones such as Guyton de Morveau, Monge, Laplace, Berthollet, and especially Fourcroy—did nothing to save him. It is said that this same Fourcroy voted for the death sentence.

Only Loysel, Cadet, Baumé, and Hallé dared to do anything. The latter sent a memorandum to the Lyceum of Arts on all the work completed by Lavoisier and on the utility which would result from it. This memorandum was read during the trial, but was of no use. It is said also by many historians and by most chemists that the ruthless tribunal which judged Lavoisier came under the influence of Marat, who had motives of hatred towards Lavoisier on account of the critique which he had written on his chemical works, especially on one entitled "Recherches physiques sur le Feu" of 1780; but this accusation is calumnious and absurd when one remembers that Marat was assassinated in July 1793, and Lavoisier was arrested in December 1793 and beheaded in May 1794 at the age of barely fifty years.

The death of Lavoisier was a disaster for the progress of science, and Lagrange said that "a single instant sufficed to make that head fall, but many centuries will not suffice to reproduce a similar one."

Lavoisier's wife, who was afterwards married to Count Rumford, collected and published the scientific memoirs of the great chemist in 1805.

[1] Later on we shall explain the significance of the words base, acid, and salt more exactly. For the present it will suffice to say that bases are ordinarily substances obtained by the oxidisation and subsequent hydration of a metal, and having the property of uniting with acids with reciprocal saturation forming salts. The bases have a so-called alkaline reaction, that is, they are able to turn red litmus paper blue in contradistinction to the reaction of the acids which turn blue litmus paper red.

More extensive and important work and exact experiments were published by Richter in 1792 to 1794 under the title "Elements of Stoichiometry, or Mensuration of the Chemical Elements." Apart from the accurate determination of the quantities of various bases which saturate the same quantity of an acid and the quantities of various acids which saturate a constant quantity of a base, he also studied gravimetrically the reciprocal action of numerous neutral salts which react with formation of other neutral salts.

For the first time in history we encounter an attempt to apply mathematics to the elucidation of chemical reactions, and from the beginning of his chemical career (1789) Richter devoted his whole activity to the discovery of the mathematical laws which regulate chemical reactions. He considered chemistry as a part of applied mathematics, and endeavoured to establish so-called arithmetical and geometrical series from which to evolve such laws. We owe to him a clear conception of chemical equivalents, which he stated concisely for salts, in the following law. *In various salts derived from the same acid, the weights of the various metals corresponding with an equal and constant quantity of the acid are represented by values which are chemically equivalent and which are constantly found again unaltered* (*or in multiples*) *in the formation of other salts ; thus also in various salts of the same metal, the quantities of the various acids corresponding with a definite weight of metal are constantly found again* (*or in multiples*) *in other salts.*

He determined, for instance, the quantities of different bases necessary to neutralise 1000 parts of sulphuric acid and these quantities he called the series of neutrality of the bases. Naturally these values were not very exact, but they possess historical importance as the first table of equivalent weights. In a similar manner he established a neutrality series for the acids known at that time. He found that, with 793 parts by weight of lime (or 672 of ammonia or 859 of soda) there corresponded 1000 parts of sulphuric acid, 577 of carbonic acid, 1405 of nitric acid, 755 of oxalic acid, etc. From these numbers it is easy to calculate the quantities of any base and any acid required to give a neutral salt.[1]

In 1803 Berthollet published a classic work entitled "Chemical Statics," in which he endeavoured to demonstrate that the variety of chemical combinations and phenomena is due to a certain fundamental and immutable property of matter, and supposed that between the particles of matter there is a certain attractive force, a certain affinity, of the same character as gravity; thus, according to him, chemical phenomena follow well-determined mechanical laws under the exclusive influence of mass and of affinity, and not, as Richter declared, in definite proportions of constant weights.

According to Berthollet, then, the quantity of one substance which combines with another varies with variations in the amount by which one or the other preponderates, in such a manner that two substances would be able to combine in very varying proportions by varying the quantity of the substances, that is, of the amount of the one or other component, but in harmony with the affinities. He believed that the reason why a mathematical explanation,

---

[1] These most interesting studies of Richter were not at that time considered to be of much importance, although he himself introduced them into his principal work in eleven volumes, published in the years 1797–1802, and although G. E. Fischer in his German translation of Berthollet's work on "Affinity" introduced the table of equivalents and the ideas deduced by Richter—ideas and values which Berthollet himself had accepted and introduced in his principal work, "Chemical Statics," in 1803. It is difficult to understand how Berzelius could attribute the origin of these studies to Wenzel. Richter himself remained neglected by others for forty years until Hess brought his work to light again in his writings in 1840. Hess was forgotten in his turn by his contemporaries, but his work was recalled by Ostwald in 1886, who proclaimed him to be the true founder of thermo-chemistry. The work of Richter did not find followers because the attention of the chemists of that time was riveted entirely on the interesting dispute, prolonged for many years, between Berthollet in France and Proust in Spain (*see later*).

such as existed for gravitation between the stars, had not yet been found, was that the distances between the particles were so small and their forms so various, that the necessary mathematical calculation became very difficult.

Proust (1801–1806) arrived by another method at the same results as Richter, and showed that there really existed a constant proportion between two elements in a compound, thus formulating for the first time the law of constant proportions. He also found that two elements are able to combine in more than one proportion, but that these proportions are always well determined and constant; for example, in the case of a metal which forms two oxides. This last observation should have led Proust to the law of multiple proportions, but this was only discovered and experimentally proved later on by Dalton, because Proust did not succeed in making the demonstration precise on account of the well-known inexactitude of his experiments and quantitative determinations.

The enormous number of analyses which led Proust with certainty to the law of constant proportions were repeated with the greatest accuracy and exactness by Berzelius, and later also by Stas. These results exactly confirmed the law of Proust.

Thus on decomposing and analysing

100 grms. of	water	one obtains	11·12	grms. of	hydrogen	and	88·88	grms. of	oxygen
,,	hydrochloric acid	,,	2·8	,,	,,	,,	97·2	,,	chlorine
,,	hydrogen sulphide	,,	5·9	,,	,,	,,	94·1	,,	sulphur
,,	lead sulphide	,,	13·4	,,	sulphur	,,	86·6	,,	lead
,,	lead chloride	,,	25·54	,,	chlorine	,,	74·46	,,	,,
,,	lead oxide	,,	92·825	,,	lead	,,	7·175	,,	oxygen
,,	ammonia	,,	17·7	,,	hydrogen	,,	82·3	,,	nitrogen

These are the direct results of the analyses, which did not apparently represent anything further, but the figures acquire a surprising eloquence if they are compared with one another, after referring them to a definite quantity of one of the components, taken as unity; thus, if we refer all these weights to an equal quantity of hydrogen and then compare these new relations, we find that one part of weight of hydrogen corresponds:

In water	with	8	parts of	oxygen
,, hydrochloric acid	,,	35·5	,,	chlorine
,, hydrogen sulphide	,,	16	,,	sulphur
,, lead sulphide, 16 parts of sulphur (= 1 hydrogen) . .	,,	103	,,	lead
,, lead chloride, 103 parts of lead (= 16 sulphur = 1 hydrogen)	,,	35·5	,,	chlorine
,, lead oxide, 103 parts of lead	,,	8	,,	oxygen
,, ammonia, 1 part of hydrogen	,,	4·67	,,	nitrogen

Now we see that the oxygen in water and in lead oxide has the same value of 8 (referred to the weight of hydrogen as one) and that the sulphur occurs in the proportions of 16 parts by weight, both in hydrogen sulphide and in lead sulphide; chlorine occurs in 35·5 parts by weight in hydrochloric acid and in lead chloride; and lead occurs in the proportion of 103 parts by weight in both the oxide and chloride of lead.

These values were called combining weights or chemical equivalents or stoichiometric values. They represent the quantities by weight of each element which correspond with or are equivalent to hydrogen taken as unity.

It is evident from these results that the principle of the law of constant proportions of Proust is exact, that is, that the elements combine with one another in constant proportions or weights, as Richter had perceived; thus 16 grms. of sulphur combine chemically with 103 grms. only of lead, even though this latter may be present in much greater quantity. The excess over and above 103 grms. remains unaltered as lead and is not transformed into sulphide.

There is, therefore, no influence of mass, as was declared by Berthollet.[1]

Whilst the dispute between Berthollet and Proust still raged, Dalton, by a brilliant conception (1800–1803–1808), succeeded in explaining simply and clearly the constant composition of chemical combinations. Starting from the hypothesis of the ancient Greek philosophers (Leucippus, Democritus, Epicurus, and Lucretius, *see* p. 12), who considered matter to be constituted of small particles, distinct from one another, he developed this hypothesis by supposing that the particles constituting a given simple substance—which he called *atoms*—were equal to one another in weight and in volume, but different from those of any other simple body; the properties or qualities of these atoms are those which determine the qualities of the substance, and these will vary as the quality of the atoms varies. By mathematical speculations and chemical determinations and experiments he was able to show that chemical compounds result from the union of two or more atoms of different kinds. From the results of his experiments, he succeeded also in determining the relative weights of these atoms, and was then able to demonstrate experimentally one of the fundamental laws of modern chemistry, namely, that of multiple proportions, which had already been suggested, but not proved, by Proust.

According to this law the atom of a given element (simple substance) can combine with 1, 2, 3, 4, etc., atoms of another element, that is, with an integral number of other atoms. Dalton deduced this important law experimentally by analysing numerous chemical compounds, and we may illustrate it by taking the combinations of nitrogen with oxygen, which give on analysis the following results:

I.	Nitrous oxide	contains	63·6	per cent. of nitrogen	and	36·4	per cent. of oxygen
II.	Nitric oxide	„	46·7	„ „	„	53·3	„ „
III.	Nitrogen trioxide	„	36·8	„ „	„	63·2	„ „
IV.	„ tetroxide	„	30·5	„ „	„	69·5	„ „
V.	„ pentoxide	„	25·9	„ „	„	74·1	„ „

On recalculating these results and referring then to the stoichiometric values or combining weight of oxygen, which we have already seen to be 8, we find that in the first compound the stoichiometric value of oxygen corresponds with 14 parts of nitrogen, that is, with three times its stoichiometric value, which we know to be 4·67.

If we now retain the 14 parts of nitrogen for the other compounds, we find

In	I.	14 parts of nitrogen combine with	8	parts of oxygen
„	II.	„ „ „ „	16	„ „
„	III.	„ „ „ „	24	„ „
„	IV.	„ „ „ „	32	„ „
„	V.	„ „ „ „	40	„ „

It is evident from these results that a given constant quantity of one element, which may be one atom, combines with a given quantity of another element (for example, one atom) or with a double, triple, or quadruple, etc., quantity, and that actually these quantities are in the proportions of the stoichiometric values or combining weights. Thus complete atoms, and not fractions of

---

[1] The hypothesis of Berthollet did not meet with success at that time, mainly because it was antagonistic to the fundamental laws discovered by Proust, Dalton, and Gay-Lussac, but eventually its application was found much later, and it became a fundamental law for the exact interpretation of all chemical reactions. The Norwegians, Guldberg and Waage, found a mathematical expression for chemical systems in reaction which replaced the conception of chemical mass of Berthollet by a more rational conception of active mass, as will be explained later.

atoms or arbitrary quantities, combine with one another. In this way the atomic hypothesis was rendered more definite and concrete, and became necessary in the contemporary state of science in order to explain chemical phenomena.

The brilliant hypothesis of Dalton was at once accepted by all the more authoritative scientists of other nations, who could only confirm its utility and importance both for chemistry and for other sciences. This hypothesis has aided the interpretation of all phenomena to such an extent that by most chemists it is considered as a true positive theory and as the basis of the chemical philosophy which has been developed in the last century.[1]

LAWS GOVERNING MATTER IN THE GASEOUS STATE

(1) THE LAW OF BOYLE AND MARIOTTE. It was the exact study of gaseous matter which first led to the discovery of the more important laws of chemistry and physics. By means of sufficiently exact instruments Galileo (1564–1642), one of the founders of the inductive and experimental method, had already succeeded in showing that the air possessed weight, and thus shattered at one blow the statement of Aristotle, who believed the air to be imponderable; all experiments up to that time had been made by weighing a bladder inflated with air and weighing it again when empty, by which means no difference in weight was found.

Torricelli (1608–1647) deduced by means of the barometer the weight of a long column of air, viz. the atmosphere. Black studied the evaporation of liquids and deduced laws which showed that in such evaporation heat is absorbed (latent heat). Priestley, who was a strenuous worker, was one of the first to introduce exact instruments for the measurement of gases, but even before this time Boyle (in 1662) and Mariotte (in 1679), by studying dry air in vessels which allowed the volume to be measured and by always keeping the temperature constant whilst they altered the pressure, arrived at an important law, namely, that the volume of a gas varies in inverse proportion to the pressure, that is to say, that the volume of a gas diminishes proportionately to the increase of pressure.

This law can be represented by a mathematical formula, in which v indicates the volume of a gas at pressure p, and v' the volume of the same gas at a different temperature, p'. As the volume of the gas is inversely proportional to the pressure, we have $v : v' = p : p'$ or $pv = p'v'$, which signifies that the product of the pressure and the volume of the same quantity of gas is always the same, so long as the changes of pressure or of volume are not accompanied by changes of temperature or of the quantity by weight of the gas.

If, for example, we have a volume of gas $v = 10$ litres at a pressure $p = 2$ atmospheres, then we have $p . v = 2 - 10 = 20$. If we now subject the same 10 litres to twice the pressure, so that $p' = 4$ atmospheres, the volume becomes halved, that is, 5 litres. Thus in this case also the product of the volume and the pressure is equal to 20 as in the first case, since $p' . v' = 4 \times 5 = 20$. Thus the product of the volume of a gas by the pressure (the temperature remaining invariable) is always constant at any pressure at any instant.

Boyle made his experiments up to pressures of four atmospheres only, but the law of Boyle and Mariotte has been confirmed by all who have since tested it.[2]

---

[1] During the last few years the atomic hypothesis has become insufficient to explain certain new phenomena, and we are at present perhaps passing through a transition period which will certainly lead to new and still vaster horizons, because the atom contains behind and within it a whole new world of marvels (*see below*, "Unity of Matter and Energy," and the chapter on Radium).

[2] Very small variations from the formula above expressed mathematically always occur, and were studied exactly by van Marum at the end of the eighteenth century in the case of ammonia gas.

Orstedt also found small differences in the case of sulphur dioxide, and in 1827 Despretz, in a numerous series of experiments, showed that the law of Boyle and Mariotte is not rigorously

We will also give the graphic representation of this important law in order to demonstrate how advantageous this method is for rendering evident the mathematical expressions of such laws, enabling us in many cases rapidly to form an exact idea of the course of a physical or chemical phenomenon even at moments or under conditions which cannot be attained or which are difficult to arrive at by mathematical calculation.

We have seen that, for a given quantity by weight of a gas, under varying pressures, the product of pressure and volume remains constant.

In the formula $p . v = C$ (constant), which represents Boyle's law, p is a function of v, and *vice versa* v is a function of p, because in general when two variable quantities are reciprocally dependent, the value of the one is determined if we know the value of the other. Thus, if for a constant value of C, namely, 100, the values of p are determined as 1, 2, 4, 10, 25, and 100, the corresponding values of v, which is a function of p, will be 100, 50, 25, 10, 4, and 1 respectively. That is, we have a *function of the second degree* which contains the product of the two quantities, so that we arrive geometrically at a *linear function* which will be represented graphically by a curve. If then we take two *orthogonal axes* (that is, axes which intersect at right angles) OV and OP (Fig. 2), and mark off points along the axis OV, the distances of which from the point O correspond with the various volumes (having once for all fixed the relation between lengths and volumes, *e. g.*, 1 mm. corresponding with 1 litre), and if we similarly mark off the corresponding pressures along the vertical axis (the axis of the ordinates) OP, then, supposing that we start with 50 litres of gas at a pressure of two atmospheres, we have a fixed point e in the plane of the paper,

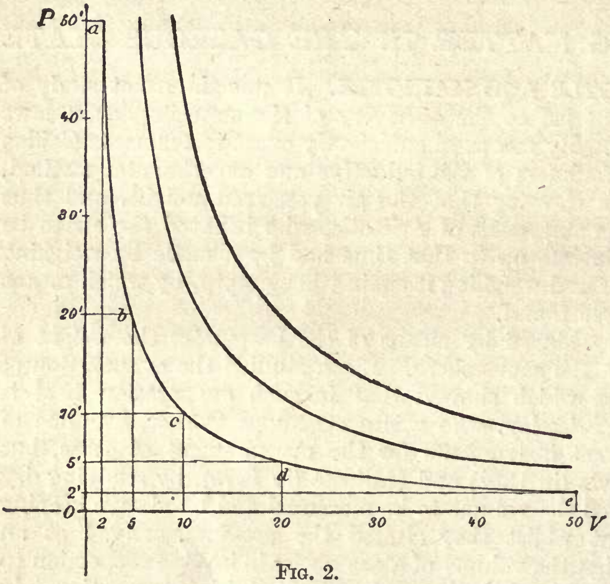


Fig. 2.

---

true for vapours or for gases at a temperature or pressure near to their point of liquefaction, whilst the so-called perfect gases such as oxygen, which are not easily liquefied, follow the said law exactly at a pressure of 15 atmospheres. Dulong and Arago showed in 1829 that up to pressures of 27 atmospheres air follows the law of Boyle very exactly. Later on, about 1850, Regnault conducted a series of most important experiments carried out with the very greatest care and with the greatest facilities, and showed that no gas rigorously follows Boyle's law, but that they can all be compressed slightly more than they should be according to theory, excepting hydrogen, which is less compressible. In 1852 Natterer found that other gases also behave like hydrogen when they are strongly compressed. In 1870, 1877, and 1879, Cailletet made extensive experiments of this kind, his results defining still more carefully the general law and its variations.

In 1880 Amagat undertook important experiments, exposing gases to very high pressures (up to 430 atmospheres) by using a steel tube 327 metres long curved into a closed U at the lower end and filled with mercury and penetrating below into a deep mine (at Meons, near St. Etienne). He fully confirmed the results of Regnault and of Natterer for highly compressed gases, and also the exceptional behaviour of hydrogen.

Amagat also found in the course of his work that the exceptions and variations from Boyle's law become less as the temperature is raised, and that for every gas a different temperature must exist at which it behaves exactly according to Boyle's law. In 1883 Amagat studied the behaviour of gases with regard to Boyle's law at small pressures less than one atmosphere, that is, he studied rarefied gases, and found that these also follow the said law exactly, thus coming to conclusions opposed to those which had been arrived at some years before by Mendeléev and Kirpitschoff.

We shall later on explain all these small variations of Boyle's law, and they will serve as a basis for most important new laws which we shall then study.

and the surface $O, V, e, 2'$ represents geometrically the constant C of Boyle's formula ($2 \times 50 = 100$); a volume of 20 litres of gas will be exposed to a pressure of 5 atmospheres, which we represent by the ordinate d, and we have now fixed another point d, the surface O, 20, d, $5'$ again representing the constant C ($5 \times 20 = 100$); under a pressure of 10 atmospheres the volume becomes 10 litres and we have fixed the point c, the constant remaining always the same ($10 \times 10 = 100$); similarly we are able to fix the point b, where the pressure is 20 atmospheres and the volume 5 litres. If we establish a sufficient number of points in this manner and then unite them with one another, we obtain a curve which will be a rectangular hyperbola, the extremities of which tend to approach indefinitely near to the respective axes, but without actually coming into contact with them (except at infinity); such a curve, which is described as asymptotic to the axes, indicates that the volume of the gas would become either zero if the pressure were infinite or infinite were the pressure to become zero. This would naturally only apply to an ideal gas (and we may consider nitrogen, oxygen, hydrogen, etc., to be practically though not absolutely ideal gases); but as we have seen, the law of Boyle has limitations, and is noticeably inaccurate in the case of vapours or of gases near their condensation point, such as ammonia, sulphur dioxide, etc. Since the formula which represents Boyle's law holds only when the temperature remains constant throughout the variations, of pressure and volume, we shall obtain other hyperbolas for other temperatures, and each of these is called an *isothermal* curve and corresponds with a definite temperature. In Fig. 2 two other isothermals, corresponding with two other temperatures, are also shown.

(2) **LAW OF GAY-LUSSAC AND DALTON.** The study of the behaviour of gases under variation of other conditions than that of pressure is also of interest. In about the year 1805 Gay-Lussac and Dalton discovered almost simultaneously that all gases dilate to an equal extent when heated, and that this dilatation is proportional to the rise of temperature. Gay-Lussac and Dalton also measured the coefficient of expansion of air and obtained the value 0·00375, but the more exact experiments of Rudberg, of Magnus, and of Regnault showed that the true coefficient of expansion of gases is 0·00367. This figure, when expressed as a fraction, is equal to $\frac{1}{273}$ and signifies that every gas increases or diminishes its volume by 1-273rd part of the volume at 0° for every degree of rise or fall of temperature. Thus if we imagine a volume of gas at 0° enclosed in a cylinder with an ideal frictionless and weightless piston, on lowering the temperature to 273° below zero the gas will diminish in volume by $\frac{1}{273}$ of its original volume (at 0°) for each degree and will thus occupy no volume whatever, that is, it will be deprived of every form of energy or matter, which is absurd; we may say more correctly that below this temperature the energy of its material will remain constant. (If temperatures below absolute zero have any meaning.—*Translator's note.*) This limiting temperature, with regard to which the common zero point of thermometers would be + 273°, is called the *absolute zero.* Thus at 272° below zero a gas would really occupy $\frac{1}{273}$ of its volume at 0°. On raising the temperature the volume will constantly increase and at 273° above absolute zero, that is, at the ordinary zero temperature, it will occupy its original volume, which is 273 times larger than the volume which it occupied at 272° below zero. Thus the volume of a gas is proportional to its absolute temperature, so that at 273° above the ordinary zero point a gas will acquire double the volume which it occupies at the ordinary zero, or 546 times its volume at − 272°.

The conception of absolute temperature is interesting also because it enables us to understand why it is impossible to transform thermal energy completely into mechanical energy. The actual mechanical work which can be produced by the interchange of heat between two substances is proportional to the temperature difference through which the transformation of heat into work occurs. The greater the difference in temperature between the two substances, the greater will be the yield of mechanical work; hence it follows that in order to transform all the heat in a body into mechanical work it would be necessary to lower its temperature to absolute zero, which is practically impossible (*see also below*, and p. 7, "Degradation of Energy").

The law of Gay-Lussac and Dalton may also be represented by a mathematical formula in which V indicates the volume of a gas at the temperature T, and V' the volume of the same weight of gas at the temperature T'; the volumes being proportional to the absolute temperatures, we have:

$$V : V' = T : T', \text{ or } V' . T = V . T', \text{ that is, } V' = \frac{V\,T'}{T}.$$

If, for example, a gas occupies a volume V of 4 litres at the temperature, T, of 300° absolute, that is, at 27° above the ordinary thermometric zero, it will occupy a volume V' of 8 litres at the temperature, T', of 600° absolute, that is, 327° above the ordinary zero; controlling this by the above formula, we have:

$$4 \times 600 = 8 \times 300$$
$$V . T' = V' . T$$

If we denote the coefficient of dilatation of gases by a, the volume of a certain quantity of gas at 0° by v_0, and that at $t°$ by v_t, we then have the equation: $v_t = v_0\,(1 + at)$, always under the condition that the pressure remains constant.

If we take the volume at 0° as 1, then at 10° v_t will be 1·0367, at 20° 1·073, at 50° 1·184, and at 100° 1·367, etc.

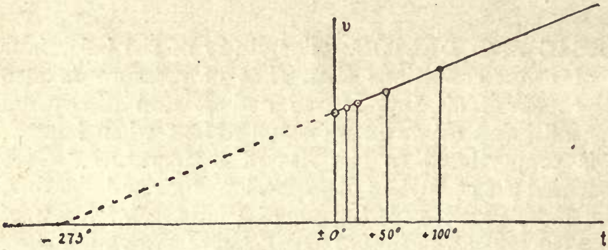


FIG. 3.

The graphic representation will be a curve of the first degree, since the two variables are always present in the first power and are not multiplied by one another, and will lead to a linear function, so that the law of Gay-Lussac and Dalton will be represented by a straight line. If we take the temperatures t as abscissæ and the volumes v as ordinates (Fig. 3), then on drawing a curve through the points representing the various volumes and the corresponding pressures we obtain a straight line, which, if prolonged in the direction of the temperatures below 0°, shows a zero volume at $-273°$.

We have seen that the formula of Gay-Lussac's law applies if the pressure of the gas remains constant during heating; if, on the other hand, the volume of the gas is kept constant while it is heated, its pressure will necessarily rise and the pressure p_t at $t°$, expressed as a function of the pressure p_o at 0°, will be $p_t = p_o\,(1 + at)$.

By combining the two expressions which represent the laws of Boyle and of Gay-Lussac, for a gas of volume v at pressure p and temperature t on the ordinary scale, we obtain the *general equation for gases*: $p . v = p_o . v_o\,(1 + at)$, or, since $a = \frac{1}{273}$, we may write $p . v = p_o . v_o\left(1 + \frac{t}{273}\right)$ and this corresponds equally with $p . v = \frac{p_o . v_o}{273}\,(273 + t)$; since the factor $273 + t$ indicates the absolute temperature T, we may write $p . v = \frac{p_o . v_o}{273}\,T$.

The factor $\frac{p_o . v_o}{273}$ has a constant value R, which is the same for all gases, whatever their chemical nature may be, if for the value v_o we select the molecular volume, that is, the volume in cubic centimetres at 0° and 760 mm. pressure of a quantity of gas equal to its molecular weight expressed in grams (gram-molecule, abbreviated to *Mol.*); the final and *general formula for gases* then becomes: $p . v = R.T.$

According to Avogadro's law the molecular volume of all perfect gases at 0° and 760 mm. pressure is always 22,412 c.c., that is, 2 grms. of hydrogen or 32 grms. of oxygen, and so on, occupy 22,412 c.c.; consequently

$$R = \frac{p_o \, . \, 22412}{273}.$$

The figure which represents the value R is, as we have said, independent of the nature of the gas, but varies with the units of measurement which we select to represent the magnitude p and the molecular volume; if we measure the pressure in units of one atmosphere ($p_o = 1$) and the molecular volume in litres (that is, 22·412 litres), then

$$R = \frac{22{\cdot}412}{273} = 0{\cdot}0821 \text{ and thus } p \, . \, v = 0{\cdot}0821 \, T.$$

If, instead, the pressure p_o, that is, one atmosphere, is expressed in grams of mercury per sq. cm. (76 c.c. of mercury = 1033·3 grms.), and the molecular volume in c.c. (22,412), then the value of the *gas constant* becomes:

$$R = \frac{1033{\cdot}3 \times 22412}{273} = 84780 \text{ and thus } p \, . \, v = 84780 \, T.$$

In the general formula for gases, $pv = RT$, we know that pv represents a quantity of energy, namely, the energy of volume, which is independent of the volume and pressure for any gas whatever and is determined solely by the absolute temperature T. That is, pv represents the quantity of energy (in absolute units)[1] necessary for the conversion of a gram-molecule of any liquid or solid substance whatever into gas (22,412 c.c.), in order to overcome the atmospheric pressure. We shall show below that the work expressed in calorific units becomes $pv = 1{\cdot}985 \, T$ calories, since a calorie corresponds with 42,720 absolute units (ergs, *see below*), and thus

$$\frac{84780}{42720} = \text{about } 2 \text{ calories.}$$

Further, since the work necessary to increase the volume of any gas by one litre, overcoming the pressure of one atmosphere, is 1,033,300 absolute units,[2] and since a calorie corresponds with 42,720 absolute units, the number of calories corresponding with the work of one litre-atmosphere will be:

$$\frac{1{,}033{,}300}{42720} = 24{\cdot}19 \text{ calories.}$$

If now in the general formula for gases (I), instead of representing p_o by unity, we represent it by the corresponding value in calories (of one litre-atmosphere), we shall have:

$$p \, . \, v = 0{\cdot}0821 \times 24{\cdot}19 \, T = 1{\cdot}985 \, T.$$

---

[1] *Absolute pressures* are pressures expressed in absolute units of the international system, the centimetre-gram-second (C.G.S.) system. The *dyne* is the unit of force which imposes an acceleration of 1 cm. per sec. per sec. on 1 grm. of matter at the sea-level at latitude 45°. It is known that gravitation produces an acceleration of 981 cm. per sec. per sec. on 1 grm. of matter, and thus a weight of 1 grm. expressed in absolute units of force corresponds with 981 dynes. The pressure of 1 atmosphere corresponds with a column of mercury 76 cm. high with a cross-section of 1 sq. cm., that is, with a weight of 1033 grms. and therefore with 981 × 1033 dynes, *i. e.*, about one million or 10^6 dynes. As the work corresponding with the unit of force (the dyne) is called the *erg* (the absolute unit of work), the pressure of an atmosphere expressed in absolute units of work will be 10^6 ergs, or, more exactly, 1,033,300 ergs. (*Translator's note.*—This should read "work done against atmospheric pressure through a distance of 1 centimetre.")

[2] If we imagine a cylinder of 1 sq. decimetre cross-section in which is a piston supporting a pressure of 1 atmosphere, then to raise the piston by 1 decimetre, that is, to increase the volume inside the cylinder by 1 litre, we must do work corresponding with the raising of 103·33 kilos through a height of 1 dm. (since the pressure of one atmosphere corresponds with 1033·3 grms. per sq. cm. and to 103·33 kilos per sq. decimetre); the work necessary to raise 103·33 kilos through a height of 1 dm. is equal to that required to raise 1 grm. through a height of 1,033,300 cms.

CRITICAL TEMPERATURES AND PRESSURES OF GASES

On compressing or cooling a gas, this is ordinarily transformed into a liquid, the molecules approaching one another owing to the pressure or to the lowering of the temperature, until they reciprocally attract one another in a stable manner. Nevertheless, some gases resist liquefaction even under the highest pressures, amounting to thousands of atmospheres, as was proved by Natterer.

At the close of 1823 Faraday found a general method of liquefying many gases, especially chlorine; into a glass tube bent into an angle and closed at one end he introduced chlorine hydrate, and then sealed the other end of the tube in the blow-pipe (Fig. 4). By immersing the end of the tube containing the crystals in a water-bath the chlorine was completely evolved at 30°, and on immersing the other end in a beaker containing ice the gas was liquefied by the strong pressure which the gas itself exerted as it was developed.

In this way Faraday succeeded in liquefying carbon dioxide, hydrogen sulphide, hydrogen chloride, sulphur dioxide, ammonia, and chlorine.

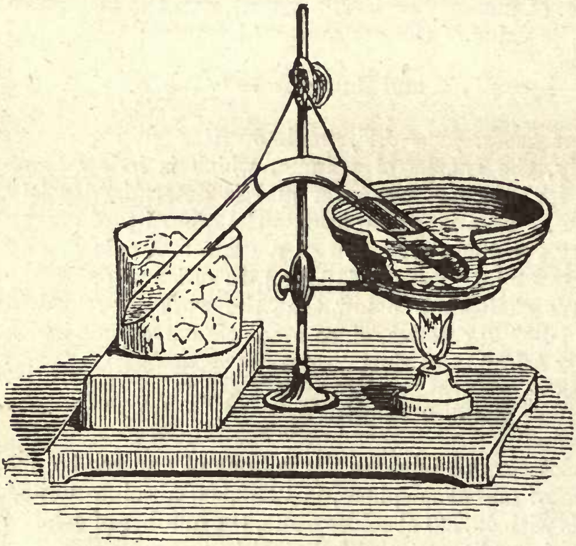


FIG. 4.

In 1835 Thilorier prepared large quantities of liquid and solid carbon dioxide. On mixing the latter with ether he obtained a temperature of 100° below zero and, by evaporating the mixture *in vacuo*, of 110°. Until 1877 it had not, however, been found possible to liquefy hydrogen, oxygen, nitrogen, carbon monoxide, air, methane, or nitric oxide, and for this reason these gases were called the *permanent gases*. In 1869 and 1872 Andrews showed, by important investigations and numerous experiments, that for gases in general a temperature exists above which they cannot be liquefied whatever the pressure may be. Thus at 0° carbon dioxide is liquefied at 35·4 atmospheres pressure, at 30° at 73 atmospheres, whilst at 31° it cannot be liquefied under any pressure. Its volume then diminishes until it corresponds with the liquid condition (critical volume), but the substance still remains gaseous. This limiting temperature, above which the liquefaction of a gas is impossible, is called its *critical temperature* (T), whilst the pressure which is necessary to liquefy it at the critical temperature is called the *critical pressure* (P).

Natanson, and, still more completely, van der Waals, obtained an equation of the third degree based on the deviations from the law of Boyle, by means of which they were able to calculate theoretically the critical temperatures and pressures of the various gases in advance, and experience has fully confirmed their deductions. On the opposite page we give the critical temperatures and pressures of a few gases.

The phenomena of the critical temperature are graphically illustrated in Fig. 5, which refers to the behaviour of carbon dioxide. If we start with a given weight of carbon dioxide and plot as abscissæ on the horizontal axis the volumes which it assumes at varying pressures and plot the corresponding pressures as ordinates on the vertical axis, we obtain for each temperature a different isothermal curve. In the first isothermal, corresponding with a temperature of 13·1°, we see that, starting from the base on the right hand, the curve rises for a short distance, because as the pressure rises the volume diminishes correspondingly; the curve then becomes rectilinear and horizontal, which indicates that the pressure remains constant while the volume rapidly diminishes; in this portion we have the gradual liquefaction of the carbon dioxide. During this transformation of vapour into liquid it is impossible to raise the pressure, as any attempt to do so simply increases the rate of liquefaction; when all the vapour is transformed into liquid we see that the volume scarcely diminishes any further, as liquids are only very slightly compressible, and thus the isothermal rises rapidly in an almost vertical direction up to the highest pressures. The next isothermal, corresponding with a temperature of 21·1°, is analogous to the preceding one, but the horizontal portion, where vapour and liquid carbon dioxide coexist, is shorter and continues to diminish in the isothermals corresponding with higher temperatures until it is reduced to a point, *K*, in the isothermal corresponding with 31·1°, and at a pressure of about 76 atmospheres. The point *K* is called the critical point and corresponds with the critical temperature, critical pressure and critical volume (that is, the volume corresponding with *K* on the axis of the abscissæ).

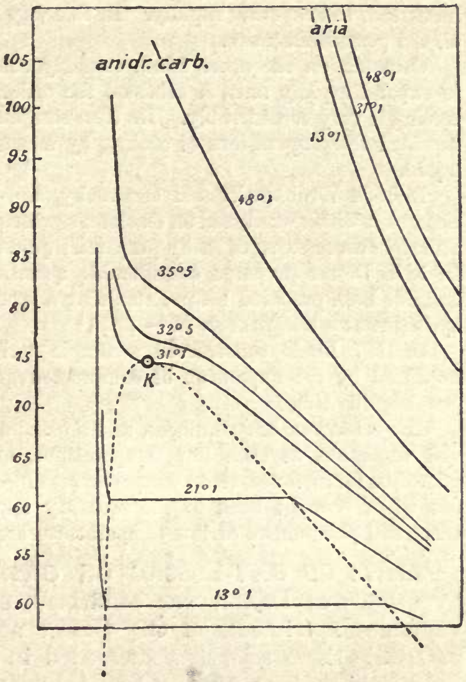


Fig. 5.

At temperatures above 31·1° it is not possible to liquefy carbon dioxide, and the isothermals corresponding with the temperatures of 32·5°, 35·5°, and 48·1° show that the curves no longer have a horizontal portion, but show, on the other hand, the passage of vapour into the state of a more perfect gas. In the right-hand top corner of the diagram three isothermals of an almost perfect gas, namely, air, which has a critical point of —140° (*see* Table), are drawn.

Gas	Critical temperature	Critical pressure : atm.	Boiling-point	Solidifying-point
Ammonia	+ 130°	115	— 33°	— 77°
Ethylene	+ 10°	52	— 102°	— 169°
Carbon dioxide	+ 31°	77	— 78·2°	— 57°
Nitrous oxide	+ 35·4°	75	— 89°	—
Nitric oxide	— 93·5°	71	— 153·6°	— 167°
Oxygen	— 118°	50	— 182·5°	— 227°
Carbon monoxide	— 139·5°	35·5	— 190°	— 212°
Air	— 140°	39	— 191°	—
Nitrogen	— 146°	35	— 194·4°	— 214°
Hydrogen	— 241°	20	— 252·6°	— 258·9°

LIQUEFACTION OF PERMANENT GASES

After the work of Andrews, Pictet at Geneva (December 22, 1877), and Cailletet at Paris (December 30, 1877), succeeded, independently of one another, in liquefying oxygen and almost all the other permanent gases. Pictet first liquefied an easily condensible gas by pressure and refrigeration; in this liquefied gas he then immersed a tube containing another compressed and refrigerated gas, and finally caused the first gas to evaporate rapidly by greatly diminishing the pressure. In this way he lowered the temperature sufficiently to produce liquefaction of the second compressed gas. In this new liquid he then immersed another strongly compressed and cooled gas, more difficult to liquefy than the preceding one, and caused this to liquefy in turn by causing the other liquefied gas, in which it was immersed, to evaporate rapidly. In this way he gradually succeeded in liquefying almost all the permanent gases.

Cailletet, on the other hand, strongly compressed a cooled gas and then allowed it to expand rapidly until it attained the ordinary pressure; he succeeded in this way in cooling it very considerably. He then compressed it again and allowed it to expand, and repeated these operations of cooling by means of expansion until he finally obtained the liquid.

In 1884 Wroblewsky and Olszewsky, and later Dewar in London, with an ingenious apparatus which was based on Cailletet's principle but allowed the gas compressed at twenty atmospheres to expand, easily prepared liquid air and oxygen, at a temperature of — 190°. In 1898 Dewar prepared considerable quantities of liquid hydrogen and helium, which had not been prepared before, attaining a temperature of — 258°, and then obtained solid hydrogen at a temperature of — 259°.[1]

In 1897 Linde constructed a simple and ingenious machine, based on the cooling produced by the expansion of compressed gases, for liquefying large quantities of air (*see* Liquid Air).

The behaviour of substances, and the chemical, physical, and vital phenomena, animal and vegetable, at such low temperatures, are interesting and often strange. Certain microbes, for instance, resist temperatures of — 190° very well and merely cease to multiply, but when brought back to the ordinary temperature resume all their vital functions. Electrical phenomena at low temperatures are also of interest (*see* Liquid Air).

LAWS OF GAY-LUSSAC ON GASEOUS COMBINATION. The brilliant hypothesis of Dalton was confirmed, and its importance increased, by the valuable experiments of Gay-Lussac and Humboldt which quickly followed in 1805; these scientists succeeded in showing that one volume of oxygen gas combines with exactly two volumes of hydrogen gas to form water. In 1808 Gay-Lussac alone, continuing these experiments on the combination of gases, found that a constant and simple relation existed not only between the volumes of gases (or vapours) which combined, but also between the total volume of the gases entering into combination and the volume in the gaseous or vaporous state of the resulting compound.

We may illustrate these important laws discovered by Gay-Lussac by a few experiments.

In order to show that water is composed of hydrogen and oxygen, it is sufficient to decompose it with an electric current in a Hofmann U-tube (Fig. 6). One end of this tube is closed, and if connected with the negative (zinc) pole of an electric battery, hydrogen will collect there whilst oxygen is developed in the open arm at the positive pole. If the current is reversed, oxygen will collect at the positive pole and hydrogen at the negative.

In order to demonstrate the nature of the two gases which are formed, the open end of the tube is filled with water, closed with the hand, and the tube reversed in such a manner as to pass the gas into the open arm. Hydrogen is then recognised by burning when lighted with a match, whilst oxygen revives the combustion of a glowing splint of wood.

Gay-Lussac's demonstration of the fact that one volume of oxygen combines with two volumes of hydrogen may be effected by means of the apparatus shown in Fig. 7.

This is a U-shaped eudiometer filled with mercury, one arm being closed above with a tap and containing two platinum poles. By running out mercury through the lower tap a measured volume of oxygen, for example, 5 c.c., is allowed to enter through the top tap, and is then mixed with a measured excess of hydrogen, for example, 20 c.c. After

---

[1] In order to measure such low temperatures Dewar used either hydrogen thermometers at constant volume, or thermo-electric couples, or electrical resistance thermometers of various metals and alloys; the last are not exact at temperatures below — 200°, whilst the first are the best. For temperatures between — 183° and — 200° oxygen thermometers based on the vapour pressure of this gas when liquefied served very well. For ordinary measurements down to — 200° pentane thermometers served sufficiently well; pentane, C_5H_{12}, obtained from the more volatile petroleum fractions, is liquid even at ordinary temperatures and remains liquid down to about — 200°.

the total volume of the mixed gases is read when the mercury in both arms of the eudiometer is at the same level, excess of mercury is poured into the open arm in order to counterbalance the pressure produced on passing an electric spark between the platinum terminals by means of four Bunsen cells and a Ruhmkorff coil.

The electric discharge causes the hydrogen and oxygen to react with momentary dilation of the excess of gas and of the water-vapour which is formed.

After the reaction, and when the apparatus has cooled, the mercury is again brought to the same level in the two arms of the eudiometer, when the remaining quantity of hydrogen is found to be 10 c.c. Thus, 5 c.c. of oxygen and 10 c.c. of hydrogen have disappeared, that is, have been transformed into liquid water. Combination has therefore taken place in the proportion of one volume of oxygen with two volumes of hydrogen, and if the water thus formed were transformed into vapour by immersing the eudiometer in a medium with a temperature above 100°, it would occupy two volumes compared with the three complete volumes of gas from which it is derived (two of hydrogen and one of oxygen, measured at the same temperature). The second consequence of the law of Gay-Lussac has thus been demonstrated, namely, that the total volume of gas formed bears a simple relation to the total volume of the component gases (two volumes of water vapour compared with three volumes of oxygen and hydrogen together).

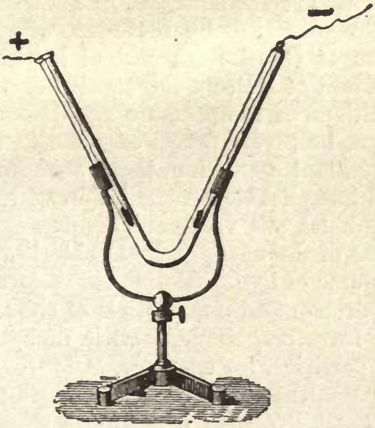


Fig. 6.

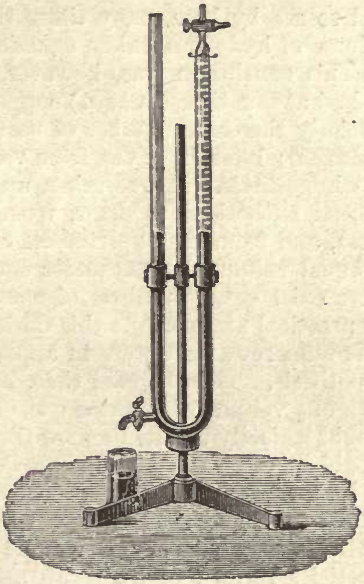


Fig. 7.

If we deduce the consequences of this experiment, we arrive at the interesting conclusion that if two volumes of hydrogen gas combine with one volume of oxygen gas in order to form water, the water must be formed according to such proportions by weight of the two components, hydrogen and oxygen, as correspond with one volume of oxygen gas and two volumes of hydrogen gas.

We have already found by means of various chemical analyses the weight of combination or stoichiometric values of the two elements, that is, we already know that in water one part by weight of hydrogen is combined with eight parts by weight of oxygen. On the other hand, we find with the balance that two litres of hydrogen (two volumes) weigh 0·18018 gr. and that one litre of oxygen (one volume) weighs 1·430 gr. The relation between these two weights is precisely 1 to 8, that is, the weight of one volume of oxygen is eight times as great as that of two volumes of hydrogen, or sixteen times as great as that of a single volume of hydrogen.

Since gases of the most diverse physical and chemical properties (both simple and compound) all follow the laws of Boyle and of Gay-Lussac, this behaviour must be regarded as due to some factor common to all gases, independently of their chemical nature. If we suppose that in equal volumes of various gases there are equal numbers of particles, and as we know that one volume of oxygen weighs sixteen times as much as one volume of hydrogen, it will follow that the particles or atoms of oxygen must weigh sixteen times as much as those of hydrogen. One litre of oxygen weighs 1·43 gr. and one litre of hydrogen 0·09 gr. The relation between these two weights is as 16 to 1, and since equal volumes will contain equal numbers of atoms, then, the atomic weight of hydrogen being 1, that of oxygen will be 16. If this reasoning were to hold for all gases, it would be possible to determine the relative weight of the particles of any gaseous substance by a very simple method. It would suffice to weigh a given volume of the gas to be studied and to see by how many times this weight is greater than that of an equal volume of hydrogen, taken as unity.

This conclusion was, however, not deduced exactly by Dalton, although he had at one time (in 1801) supposed that a given volume of oxygen contains precisely the same number of particles (Dalton atoms) as an equal volume of hydrogen; later, however, from various atomistic considerations, he abandoned this hypothesis. It was taken up about the year 1810 by Berzelius, who felt himself authorised to draw, from the laws of Gay-Lussac and of Boyle on gases, and from the experiments of Proust and of Dalton, the conclusion that in equal volumes of gas under equal conditions of temperature and pressure, there exist equal numbers of *atoms;* when, however, Berzelius came to test by practical experiments this daring and brilliant deduction, he at once found that numerous facts were in apparent and inexplicable contradiction with his hypothesis. Thus he said that, if one combines one volume of hydrogen gas with one volume of chlorine gas, one volume of the new gas, hydrochloric acid, should logically result, because the new volume of hydrochloric acid so formed should be constituted of one particle of hydrogen and one particle of chlorine, so that the two reacting particles should form one single particle of hydrochloric acid, and thus the two volumes of particles, for example, 1000 + 1000 particles, should give one volume only or 1000 particles of hydrochloric acid (particles formed of hydrogen and chlorine). Practical experiment showed, on the contrary, that two volumes of hydrochloric acid gas were formed. Further, on combining two volumes of hydrogen with one of oxygen, a single volume of water vapour should result, because each particle of water necessarily requires three particles of the constituent elements, one particle of one volume of hydrogen uniting with another particle of the second volume of hydrogen and with one particle of the volume of oxygen to give a single particle of water; thus, three volumes should form a single volume, whereas it is actually found that two volumes result.

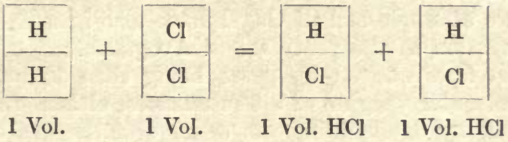
Confronted with this abnormality, Berzelius wavered, and, not being able to explain the enigma, finished partly by renouncing his hypothesis and limiting it to the simple gases, and by no longer applying it to gases formed of different elements or atoms.

Nevertheless, an Italian physicist, Count Amedeo Avogadro (1776–1856), in 1811 brilliantly explained this apparent contradiction by means of an ingenious hypothesis, which he amplified and confirmed in 1814. He supposed that the particles which we imagine to constitute matter are composed of still smaller particles, and he termed the first *molecules* and the second *atoms.* The latter are not free, but are united in pairs or larger numbers with one another in order to form molecules, which, on the other hand, exist uncombined in gases.

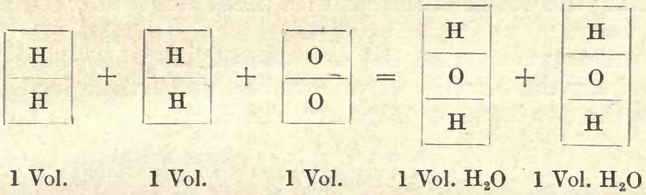
When chemical combination occurs under the influence of special circumstances, the molecules split and momentarily liberate atoms, by which means it becomes possible for these to combine with other atoms of different character, so creating new molecules of a new compound.

If we represent these molecules graphically, divided into two parts (the atoms), then the chemical reaction in respect to the volumes of gas and to the number of small and large particles (atoms and molecules) may be imagined with the help of the following figures, which indicate the atoms of hydrogen with the letter H, those of chlorine with the letters Cl, of oxygen with the letter O, hydrochloric acid with HCl, and water with H_2O.

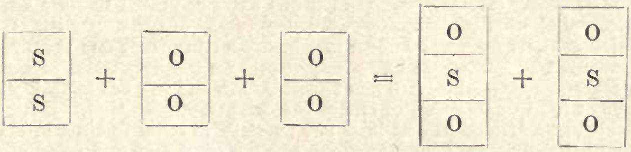
I.



II.



In this way the reactions which occur in practice are explained without any anomaly and in full conformity with the law of Gay-Lussac. We can now state with the greatest exactitude that in equal volumes of gas equal numbers of molecules (not of atoms) are contained. With the help of this conception it is also possible to foresee and establish *a priori*, in the greater number of cases, how many volumes of the gaseous compound will result from the action of given volumes of simple gases; thus, for example, it is known that if one volume of sulphur combines with two volumes of oxygen to give sulphur dioxide, the volume occupied by this new gas should be two volumes. Thus:



Avogadro[1] thus clearly deduced from the available evidence the idea

---

[1] We think it will be of interest to give a biographical note of this Italian scientist, who was for a long time unrecognised and who did so much for the progress of chemistry. Count Amedeo Avogadro was born at Turin on August 9, 1776, and died there on July 9, 1856. In 1796 he was a doctor of law, and in 1806 a teacher of physics in a college at Turin. From 1809 until 1820 he was professor of physics and philosophy at the gymnasium at Vercelli, and later was nominated professor of mathematical physics in the University of Turin. His chair was suppressed after the revolutionary movement of 1821, and he then devoted himself to the magistracy, but soon returned (in 1833) to the study of physics in the same university. He was little known in Italy and still less abroad.

His important work appeared on July 14, 1811, in the *Journal de Physique*, and the second part in 1814 in the same journal under the title " Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps et les proportions selon lesquelles elles entrent dans les combinaisons." From the law of Boyle and of Gay-Lussac he deduced that equal volumes of any gas whatsoever contain equal numbers of particles, which are present at such a distance from one another that they no longer exert mutual attraction; these particles he called *constituent molecules* or *integrants*. These molecules were formed in their turn of still smaller indivisible particles called *elementary molecules* (atoms).

Avogadro's hypothesis was not accepted at that time on account of the apparent difficulties that *equal volumes of gas under similar conditions of temperature and pressure contain equal numbers of molecules*, and it being known also that the ratio between the combining weights (stoichiometric values) is equal to the ratio between the weights of the volumes of gases which combine, the conclusion is arrived at that the ratio between the weight of one volume of any gas and the weight of an equal volume of hydrogen gas will be the same as that which exists between the weight of one molecule of the gas and that of a molecule of hydrogen.

Thus, in order to know the molecular weight of any gas, it is sufficient to know the weight of a given volume of hydrogen gas and that of an equal volume of the gas under consideration.

Thus the laws of Boyle and of Gay-Lussac also found their most beautiful and simple expression in the postulate of Avogadro.

The principal laws obeyed by gases being then known, it was easy to arrive at the molecular weights of all substances, either gaseous or capable of being evaporated, by determining the density of the gas or vapour, that is, by comparing the weight of the gas with that of an equal weight of hydrogen, taken as unity.

We shall now summarise the various methods which have been devised for determining the densities of vapours and gases, these having contributed greatly to the development of modern chemistry.

DETERMINATION OF THE DENSITIES OF VAPOURS AND GASES

The density of a gas is given by the ratio of the weight of a given volume of the gas to that of an equal volume of air, measured under the same conditions and taken as the unit of comparison. It would be more rational to refer the density of gases to that of hydrogen.

---

of imagining particles of simple gases equal to those of compound gases, whilst according to Avogadro himself a difference existed between the molecules of simple gases and those of gaseous compounds. The former were constituted of at least two similar indivisible particles—the "elementary molecules" (atoms)—which held one another united to form the free molecules, whilst the molecules of other combinations were also formed of two atoms but of different nature. He demonstrated that no case was known in which, starting from one volume of a gas B, one volume of a gas AB was formed, as one would expect on the hypothesis of the indivisibility of molecules (to-day some cases of monatomic molecules are known), but in reality a volume results which is always at least double that of one of the components, so that it is necessary that such a component should be divided into at least two particles in order to enter into a double number of new particles. He thus explained how one volume of H and one volume of Cl could form two volumes of HCl, thus explaining in an ingenious manner all the gaseous combinations known in his time.

In 1812 Davy made a vague reference to the probability of the atoms first uniting into groups which constituted the chemical particles of a substance; in 1814 Ampère clarified and amplified Davy's conception, approaching closely to the conception already fully explained by Avogadro.

There were, however, individual facts which could be explained only by Avogadro's hypothesis, but these facts were not sufficiently numerous to make the need of the new hypothesis felt by all, and it remained neglected and obscured for about fifty years, although Berzelius noted it in his treatise on chemistry and Dumas also in 1826 in his "Memoirs on certain points of the atomic theory." Avogadro's hypothesis was again brought up about the year 1850 through the new and important work in organic chemistry initiated by Gerhardt and Laurent. Gerhardt considered it as a scientific necessity in order to explain all chemical phenomena. In 1856, whilst the dispute on this hypothesis still raged, Clausius, starting from purely physical considerations, developed the mechanical theory of heat with its help.

It was the great merit of Cannizzaro to have co-operated with enthusiasm since 1858 in the propagation in Italy of Avogadro's important postulate, and to have placed the atomic theory on a firm basis and given a brilliant and synthetic explanation of it in a most valuable monograph entitled "Sunto di un corso di filosofia chimica" ("Synopsis of a Course of Chemical Philosophy"). As Lothar Meyer has said, the veil then fell from the eyes of chemists and all saw clearly in this chaos of equivalents, atoms and molecules, while Mendeléev was enabled to place on a sound foundation his periodic system of the elements (1859).

The gases must be compared at the same temperature and pressure, and it is convenient to compare all gas volumes at 0° (V_0) and at the normal pressure of 760 mm. Then, by combining the two formulæ representing the laws of Boyle and of Gay-Lussac respectively (*see* pp. 22–25) and noting the coefficient of dilatation of gases, we arrive at a single general formula:

$$V_o = \frac{V\,(p-h)}{760\,(1+0{\cdot}00367\,t)},$$

where V indicates the volume of gas at the temperature t and pressure d observed in mm. by the mercury barometer. It is, however, necessary to take into account the vapour pressures of the liquids over which the gases are measured; the pressures, h, for water are indicated in the table given in the chapter on Water.

There are various methods of determining the densities or specific weights of gases and vapours, but in all these it is necessary to take into account the observation of Amagat, that gases and vapours follow the laws of Boyle and of Gay-Lussac the more exactly, the further the vapour is removed from the temperature of condensation or liquefaction, that is, the hotter it is.

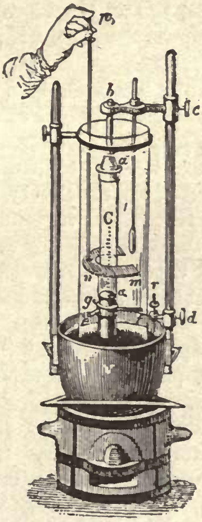


FIG. 8.

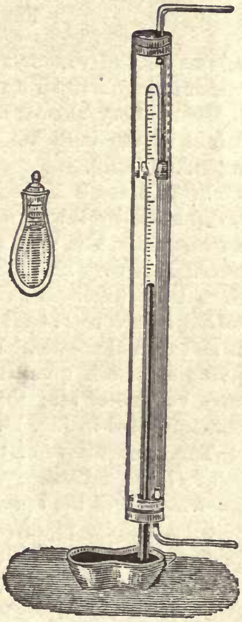


FIG. 9.

Gay-Lussac's Method (1816). A weighed quantity of a liquid or solid substance is introduced into a graduated glass tube (*see* Fig. 8) full of mercury and standing in a bath of mercury. The tube is surrounded by a large glass cylinder in which is placed a liquid (water, oil, etc.) which boils at a temperature higher than the point of ebullition of the substance under examination. The outer liquid is then boiled by raising the mercury to a sufficiently high temperature and the amount of vapour formed by the substance under examination is then measured, the temperature and pressure to which it is subjected being also noted.

A. W. Hofmann's Method (1868). This is an improvement on Gay-Lussac's method, because the graduated tube containing the mercury is 1 m. high (Fig. 9), and the substance can thus be evaporated in a barometric vacuum. We are thus able to study, undecomposed and in a state of vapour, those substances which decompose on boiling at the ordinary pressure. The substance is heated by the vapour of substances boiling in the outer tube at a considerably higher temperature than the product under examination.

Dumas' Method (1827). A weighed glass bulb of about 500 c.c. capacity, furnished with a capillary neck, is heated and the capillary immersed in the liquid (or, if a solid, molten) substance which is to be studied. On cooling, about 5 to 10 grms. of the substance are allowed to enter the bulb. The bulb is then immersed in a bath heated to a temperature higher than the boiling-point of the substance under examination. This then gradually evaporates, driving all the air out of the bulb, and when it is completely evaporated and no further vapour issues from the point of the capillary, the latter is sealed in the blowpipe and the temperature of the bath (which should be equal to that of the vapour filling the bulb) is measured, and also the height of the barometer. The bulb is well cleaned, carefully weighed, and the point then immersed in a vessel of mercury; on breaking the closed point the mercury enters and fills the bulb completely, as a vacuum has been formed by the condensation of the vapour. This mercury is then either poured into a graduated cylinder where it is exactly measured, or weighed. We have thus all the data for calculating: (1) the weight of the bulb full of air at a certain pressure and temperature; (2) the volume of the bulb at that same temperature (deduced from the volume of the mercury); (3) the volume of the air and its corresponding weight (found from a suitable table); (4) the volume of the air at the temperature of the heated vapour (calculated by means of the coefficient of the dilatation of gases, 0·00367), and thus also the volume of the vapour at the same temperature; (5) the weight of the evacuated bulb without air (obtained by deducting from the weight of the bulb filled with mercury that of the mercury alone); and (6) the weight of vapour contained in the heated bulb (the weight of the bulb full of vapour less the weight of the evacuated bulb).

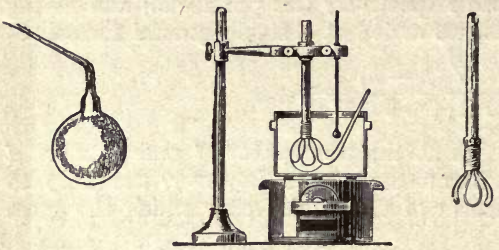


FIG. 10.

Victor Meyer's Method (1878). The volume of air which is displaced by the vapour of a given weight of substance is measured. The weighed substance under examination is placed in a very small tube and is dropped into a vertical glass tube which is provided with a delivery tube and heated to a constant temperature by hot vapours produced in an external mantle. It is there immediately evaporated, giving a certain quantity of vapour, which displaces the same volume of air; this is collected in a graduated tube, as is indicated in Fig. 11.

The temperature of the vapour is given by the boiling-point of the substance which produces the vapour in the outer mantle of the apparatus.

This simple, rapid, and exact method is one of the most widely diffused in chemical laboratories. In the case of substances which evaporate at high temperatures vessels of porcelain or of platinum are employed which are heated in furnaces or in some other manner. Exact determinations can be made with as little as 0·1 grm. of substance.

In some cases various other methods of determining molecular weights of gases are used, but none of them is in current use in laboratories, although they sometimes serve as methods of control. Among these are the methods of Wrede Svanberg (1846), Buff (1831), Marchand (1848), Pfaundler (1879), Malfatti-Schoop (1886), etc.

Some substances or elements cannot be transformed into vapour, and the molecular weight must then be determined indirectly by determining that of some volatile derivative. For instance, ferric chloride can be evaporated and from its vapour density the atomic weights of the components can be calculated. In some cases the inevitable errors must be corrected by means of the stoichiometric values which, as we have seen, stand in simple relationship to the atomic weights. Thus, if in a given compound we find the resulting molecular value of oxygen to be 32·7 we must correct it, as it must be an exact multiple of the stoichiometric value of 8, and therefore 32.

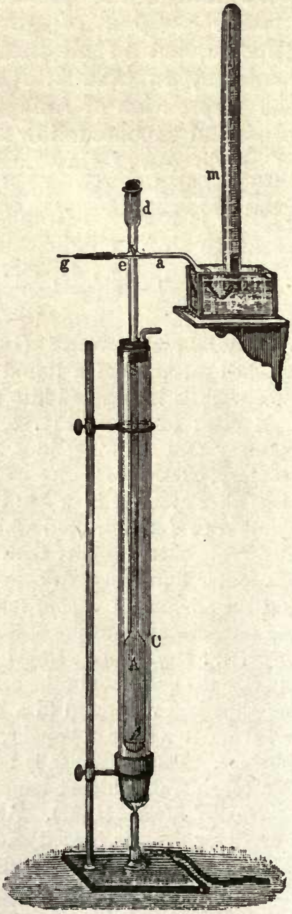


FIG. 11.

We will now consider some simple examples of the calculation of molecular weights. We know from the work of Gay-Lussac that one volume of oxygen combines with two volumes of hydrogen, and that this volume of oxygen weighs eight times as much as the two volumes of hydrogen, that is to say, a single volume of hydrogen weighs sixteen times less than the same volume of oxygen. Hence, if we take the atomic weight of hydrogen as unity, an atom of oxygen will weigh 16, because in equal volumes of gases there are equal numbers of particles (in this case diatomic molecules):

1 litre of hydrogen weighs 0·09009 grm., and if we take the weight of hydrogen as unity,
then 1 litre of chlorine weighs 3·175 grms., that is, 35·5 times as much as hydrogen;
1 litre of oxygen weighs 1·430 grm., that is, 16 times as much as hydrogen;
1 litre of nitrogen weighs 1·257 grm., that is, 14 times as much as hydrogen.

In this way we know that for elementary or simple substances, if the atom of hydrogen weighs 1, that of chlorine weighs 35·5, that of oxygen 16, and that of nitrogen 14, etc. If, instead of the relative atomic weight, we wish to know that of the molecules—as it is really these which move freely in the gas—it is seen that the diatomic molecules of hydrogen will weigh 2, of oxygen 32, of chlorine 71, of nitrogen 28, that is to say, double as much as the atoms. Ordinarily, for convenience and exactness, the density of gases or vapours is referred to that of air, that is, the weight of one litre of the gas or vapour is compared with the weight of one litre of air, taken as unity.

Since one litre of air (1·294 grm.) weighs 14·44 times as much as one litre of hydrogen (0·09 grm.), if we would have the atomic weight of the substance under examination referred to hydrogen as unity, we must multiply the density of the gas, referred to air as unity, by 14·44, and if we would have the molecular weight (where there are two atoms in a molecule) we must multiply by 28·88.

For example, the density of sulphur dioxide compared with air was found to be 2·21. On multiplying this number by 28·88, one obtains 64, which, in fact, represents the molecular weight of sulphur dioxide.

Consequently, if we know the molecular weight of a substance we can easily and *a priori* find the density of its vapours referred to air, by dividing the molecular weight by 28·88.

KINETIC THEORY OF GASES

As soon as the molecular weights were first studied, it was observed that some substances did not give results concordant with their vapour densities. For example, ammonium carbonate, ammonium chloride, and phosphorus pentachloride (PCl_5), give vapour densities, compared with hydrogen, which lead to values for the molecular weights which are one-half of those deduced from analyses and other determinations. For many years these substances were considered as true exceptions to Avogadro's law, since, as they were compound substances, it appeared absurd to imagine them as monatomic molecules (*see below*).

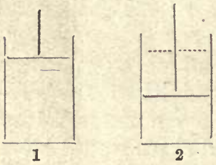
In order to explain these important exceptions, it became necessary to study the intimate nature of gases and of the particles which composed them still more attentively, and from first principles. It was the kinetic theory of gases which indirectly and by means of quite different considerations gave a new mathematical explanation of the laws of Boyle and of Gay-Lussac.

It was the work of Bernouilli (1738), a physicist of Basle, of Herapath (1821), of Joule (1851), and to a greater degree of Krönig in 1856, and more especially of Clausius in 1857, which led to the explanation of these exceptions by means of a rational mathematical theory on the nature of the pressure exercised by gases.

On what does the pressure which compressed gases exercise on the containing vessel depend, and to what is it due?

Newton believed that the pressure which is produced or exercised by compressed gases on the walls of the containing vessel was due to the action of repulsive forces which the gaseous particles exercised on one another. Bernouilli and his successors demonstrated that this hypothesis was erroneous and untenable, because if the gaseous particles were endowed with this repulsive force, then in expanding freely without doing work this force should be transformed into heat; thus, on expanding, a gas should become hot.[1] In practice the exact opposite occurs, a gas which expands greatly becoming strongly cooled, as was shown by Joule and Thomson.

Bernouilli and his successors supposed, on the other hand, that the particles of gases are endowed with rectilinear motion, and that they collide with one another and more especially with the walls of the containing vessel. The sum of these impacts with the walls of the containing vessel causes the pressure. The number of such impacts is proportional to the velocity of the particles and inversely proportional to the distance between the walls, and the result of the impacts is in direct proportion to the mass.



If then the particles contained in a given volume collide a given number of times in unit of time with the walls of the containing vessel 1, and if we now compress the gas to half the volume (vessel 2), the velocity remaining constant, then the particles will collide twice as many times against the walls in unit of time because they now have half the distance to traverse. Thus, they will exercise twice the pressure. This fully confirms Boyle's law. Actually, if n molecules are contained in a cube with side l, in order to determine the pressure which all these molecules exercise on the walls per unit of time, we must multiply the effect produced by the impact of one molecule by the number of impacts and by the total number of molecules. The molecules of mass m and velocity c will collide in various ways and at different inclinations with the several walls of the cube, and therefore, by one of the laws of mechanics, we may resolve the velocity of each single molecule, whatever its direction, into three components, u, v, z, mutually perpendicular and parallel to the sides of the cube, and we may then imagine that of all the n molecules, one-third move with a uniform velocity in one of these three senses, and two-thirds in the other two senses, colliding perpendicularly with the walls of the cube. The time taken by a molecule to travel from one wall to the other through the distance l and to return to its point of departure will be $\frac{2l}{u}$, and thus the resulting number of impacts in one second will be $\frac{u}{2l}$. The effect produced on the walls by each impact is represented by twice the quantity of motion, mu, because the molecule first collides with the wall and then turns back (we suppose the wall to be perfectly elastic and able to reverse the sense of the velocity); thus we have for each impact $2\,mu$ per second, and the effect produced on the wall by one molecule will be $\frac{u}{2l}2mu = \frac{mu^2}{l}$. Since on each wall we have the impacts of one-third of the molecules, the effect of this third will be $\frac{1}{3}n\frac{mu^2}{l}$. In order to find the pressure exercised on unit surface, we must divide by the surface of the wall (l^2), and we then have $p = \frac{1}{3}n\frac{mu^2}{l^3}$, and taking the same expression for the other molecules which move in the directions of the other components, we arrive at equal values for the velocities v^2 and z^2. For the sum of these squares of the components, $u^2 + v^2 + z^2$, we may substitute c^2, and since l^3 is simply the volume, the final expression will be $p = \frac{1}{3}n\frac{mc^2}{v}$ or $p \cdot v = \frac{1}{3}nmc^2$. This equation, which was deduced by Clausius and Krönig, represents

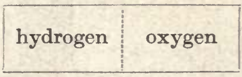
---

[1] *Translator's note.*—There is some lack of clearness here. Actually the work done would absorb heat from the gas itself and render it *cooler*.

another expression of Boyle's law. In many cases it is convenient to use another expression corresponding with the kinetic energy, viz., $p \,.\, v = \frac{2}{3} n \frac{mc^2}{2}$, and as $n \frac{mc^2}{2}$ is the kinetic energy, we may say that, *in a gas, the product of the pressure and the volume is equal to two-thirds of the kinetic energy of its molecules.* From the general gas formula, $p \,.\, v = RT$ (p. 26), we obtain the expression $RT = \frac{2}{3} n \frac{mc^2}{2}$, or $n \frac{mc^2}{2} = \frac{3}{2} RT$, and therefore we may say that the absolute temperature T is proportional to the kinetic energy (molecular translation). When $T = 0$ (absolute zero) the kinetic energy of the molecules will become zero, that is, at 273° below zero we have no longer any motion or any heat.

If we represent equal volumes of two different gases under the same condition of temperature and pressure by the general gas formula, which we have deduced above, and which comprises the laws of Boyle and of Gay-Lussac, we have in the one case, $pv = \frac{2}{3} n \frac{mc^2}{2}$, and in the other, $p'v' = \frac{2}{3} n' \frac{m'c'^2}{2}$, where n, n', m, m' are the numbers and masses respectively of the molecules of the two gases. These being under the same conditions of temperature, pressure, and volume, we have $pv = p'v'$ and hence $\frac{2}{3} n' \frac{m'c'^2}{2} = \frac{2}{3} n \frac{mc^2}{2}$ or $n' \frac{m'c'^2}{2} = n \frac{mc^2}{2}$. When the temperature of a gas falls, the kinetic energy $\frac{mc^2}{2}$ alone changes, but not the number of the molecules. Since these two gases have the same temperature and pressure, their respective kinetic energies will be equal, that is, $\frac{m'c'^2}{2} = \frac{mc^2}{2}$, and elimination of these from the preceding equation gives the result, $n = n'$. This is nothing but a demonstration of Avogadro's law, according to which equal volumes of two gases under the same conditions of temperature and pressure contain equal numbers of molecules.

We have seen that the kinetic energies of the molecules of two gases under the same conditions are identical, that is, $\frac{mc^2}{2} = \frac{m'c'^2}{2}$. From this equation it follows that $c^2 : c'^2 = m' : m$, i. e., the *squares of the velocities of the molecules of a gas are in inverse ratio to their masses* (the greater the mass the less the velocity), or again: $c : c' = \sqrt{m'} : \sqrt{m}$, which is to say that *the molecular velocities of gases are in the inverse ratio of the square roots of the masses of their molecules* (or molecular weights). Since, on raising the temperature, the number, n, of the molecules remains constant and the mass, m or m', is also constant, the kinetic energy of a gas can be increased only as a result of an increase in the velocity, c, of the particles. When a gas is heated the velocity of its particles increases, and if the volume is maintained constant, these will collide more frequently with the walls of the containing vessel, and thus the pressure will be increased; this is in agreement with Gay-Lussac's law.

We have seen that, the less the gas particles weigh, the more rapidly they move. Now, if we imagine two closed vessels, one containing hydrogen and the other oxygen, divided by a porous partition with pores sufficiently large to allow the molecules to pass through them, 

, since the hydrogen molecule is the lighter it moves the more rapidly and will thus collide a larger number of times than the oxygen molecule with the porous partition, and will pass through the pores the more easily; more hydrogen molecules will pass into the vessel containing oxygen than oxygen molecules into the vessel of hydrogen.

Since, however, the volume of the vessel containing the oxygen remains constant, if at a certain moment it contains a larger number of molecules on account of the more rapid diffusion of the hydrogen, the pressure should be increased. That this phenomenon actually occurs may be shown with the following apparatus.

A two-necked Woulf's bottle, W, contains water into which a tube dips, passing through a stopper and terminating above in a capillary tube. The other neck carries through the stopper a long glass tube, which does not dip into the liquid and terminates at the top in a closed porous cell of porcelain (porous cell of a battery), *T*. If this cylinder, which is full of air, is covered with a bell-jar, *d*, into which hydrogen passes by way of the tube, *h*, the pressure inside the porous cell immediately increases and is transmitted to the liquid by means of the glass tube, driving the water up the capillary tube and producing a little fountain, as is seen in Fig. 12. There are also small pieces of apparatus (Ansell's apparatus) which illustrate the phenomena of diffusion by ringing a bell (*see later*, Carbon Dioxide).

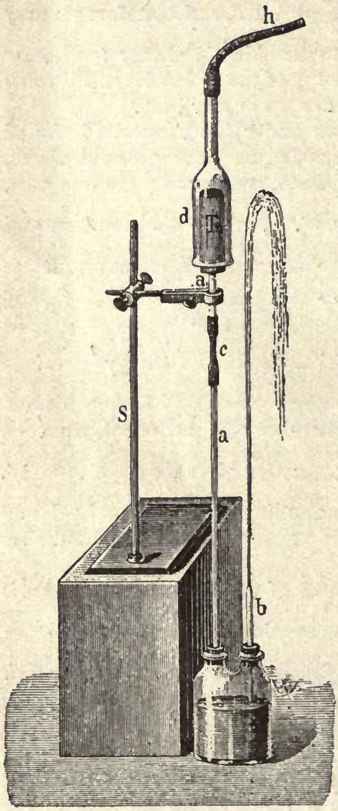


FIG. 12.

We have deduced from the kinetic theory of gases a simple mathematical formula showing that the velocities of the molecules are inversely proportional to the square roots of their weights:—$c : c' = \sqrt{m'} : \sqrt{m}$; if, for example, we suppose the molecular weight of hydrogen (H_2) to be 2 and that of oxygen (O_2) to be 32, we find that the velocity of the hydrogen molecule will be four times as great as that of the oxygen molecule, because $c\,(H_2) : c'(O_2) = \sqrt{32} : \sqrt{2} = 5{\cdot}65 : 1{\cdot}414 = 4 : 1$.

Graham also showed practically the truth of this deduction, and in 1857 Bunsen applied it to the determination of the molecular weights of various gaseous substances, using minimum quantities and simply measuring the time taken by two equal volumes of gas under the same conditions of temperature and pressure to pass through a very small perforation, scarcely perceptible to the naked eye, in a platinum plate.

The gas under experiment is enclosed in a tube inverted over mercury. This carries at the top a platinum plate with a small hole which permits the gas to escape under the pressure of the external column of mercury. By means of a glass float, the exact volume of gas which escapes in a given time may be read from a distance. This effusiometer of Bunsen is illustrated in Fig. 13. By introducing the factor of time into the general formula in place of the velocity, and taking into account that the lighter the gas the less will be the time taken in escaping, it is easy to deduce the molecular weight. The velocity of the molecule has been calculated to be 461 metres per second for oxygen, 1844 metres per second for hydrogen, 392 metres per second for chlorine, etc.

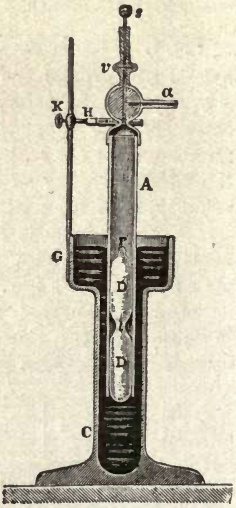


FIG. 13.

Bearing in mind these new ideas on the behaviour of gases, we may return to the determination of molecular weights by means of vapour densities in order to explain those exceptional substances, such as ammonium chloride, etc., with which molecular weights only one-half as great as the true values are obtained.

Early in 1857 St. Claire Deville made important experiments on certain decompositions occurring in various substances at high temperatures, and observed that the degree of dissociation is always the same for a given temperature and pressure. He applied the laws of thermodynamics to the study of chemical equilibria, thus anticipating by thirty years the deductions arrived at by modern chemists. In the same year, 1857, Cannizzaro and, immediately afterwards, Kopp and Kekulé (1858) showed that a molecule of ammonium chloride (NH_4Cl) dissociates at high temperatures into two new molecules, namely, into ammonia (NH_3) and hydrogen chloride (HCl), the reason why the molecular weight became halved being thus explained. For some years the discussion continued as to whether this theoretical deduction was really possible, that is, whether two such substances as ammonia and hydrogen chloride, which have very great affinity for one another, are able to exist together at high temperatures without combination.

The question was experimentally solved in an elegant manner in 1862 by Pebal and in 1864 by Than, who demonstrated the dissociation of ammonium chloride by means of the varying velocities of the molecules of hydrogen chloride and of ammonia on diffusion.

Thus, on heating a little ammonium chloride in a long open inclined tube, which is divided at about the middle by a plug of asbestos, the ammonia particles diffuse the more rapidly and are able to turn red litmus paper blue if it is placed at the further extremity of the tube, whilst in the lower portion of the tube blue litmus paper is turned red by the action of the heavier molecules of hydrogen chloride.

After this demonstration that the molecules of compounds can be dissociated at high temperatures, and since it was known that monatomic molecules of simple substances do exist (metals in the state of vapour, argon, etc.), the question arose whether the diatomic molecules of simple substances could be dissociated into free atoms. Victor Meyer and others have actually demonstrated that bromine is constituted of diatomic molecules at 228°, whilst at 1260° its dissociation into monatomic molecules is almost complete; elementary iodine is formed of diatomic molecules at 253°, whilst at 1500° it consists almost exclusively of monatomic molecules.

EXCEPTIONS TO BOYLE'S LAW—NEW EQUATION OF VAN DER WAALS—SIZE OF THE MOLECULES

Having thus explained in a plausible manner the apparent exceptions to Avogadro's law, we shall now study the deviations from Boyle's law which occur when gases are highly compressed.

In 1852 Natterer exposed oxygen and air to pressures up to 3600 atmospheres, and found that the compressibility at increased pressures is somewhat less than that required by Boyle's law, as Regnault had also observed in 1850 in the case of hydrogen even under normal conditions.

By means of the kinetic theory of gases we are able easily to explain this apparent abnormality. In calculating the compression of gases by the mathematical formulæ, we do not consider the space occupied by the molecules themselves, and consisting of their sphere of action or of vibration, into which another molecule is unable to penetrate. The distance traversed by each molecule of gas to collide with the walls of the vessel in which it is enclosed must be diminished by the radius of the molecule and its sphere of action. When considering ordinary pressures, these radii are negligible compared with the distances between the molecules, and Boyle's law remains uninfluenced. When, however, gases are strongly compressed and thus occupy relatively small volumes, the volumes of the molecules exert an influence and produce the small deflections from Boyle's law observed in compressed gases.

It has actually been proved that with pressures of 30 to 125 atmospheres, gases are generally compressed a little more than is required by Boyle's law, and that at higher pressures than these they are compressed a little less than the ordinary theory requires. Hydrogen, on the other hand, approaches more nearly than the other gases to the behaviour of an ideal gas. The first phase of greater compressibility is explained by the fact that, as the molecules approach one another they also attract one another a little, and thus the pressure which we read on the manometer is less than it would have been if this attraction did not exist. The true pressure would, therefore, be $p + \frac{a}{v^2}$, where a represents a constant which measures the reciprocal attraction of the molecules, this attraction being directly proportional to the square of the density of the gas, and, therefore, inversely proportional to the square of the volume. In gases which are strongly compressed, for example, under a pressure of more than 200 atmospheres, it is necessary, on the other hand, to take account of the volume occupied by the mass of the molecules themselves; the true free volume is thus a little less than that which is measured (that is, $v - b$). The general formula for the gaseous state, $p \cdot v = RT$, must therefore be altered, according to Van der Waals, in the following manner: $\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$.

Van der Waals and Clausius, taking the above data into account, calculated the value of the magnitude, b, of this formula from the specific volumes,[1] absolute pressures, etc. The value of the diameter of a hydrogen molecule resulting from these calculations was $1{\cdot}6 \times 10^{-8}$ cm., so that the number of hydrogen molecules contained in 1 c.c. would amount to 5×10^{19}, while a spherule of $\frac{1}{100}$ mm. diameter would contain fifty million molecules of hydrogen.

Whereas, until a few years ago, there existed a tendency (resulting especially from W. Ostwald's work) to replace the molecular conception of matter by that of the continuous energetic constitution (analogous to the old idea of homeomeria [*see* p. 12]), facts have been accumulated within recent years leading to the acceptation of the actual existence of the molecules.

From investigations dealing with the phenomena of the absorption and diffusion of light in colloidal and molecular solutions, with Brownian movements, etc., the true magnitudes of the molecules have been established. The values thus obtained coincide with those given by calculations based on the kinetic theory of gases; Rutherford, for instance, finds the diameter of the molecule to be 10^{-8} cm.

SYMBOLS AND CHEMICAL FORMULÆ

In order to represent the elements it was found useful to abbreviate graphic expressions by employing symbols.

The ancients, and still more the alchemists, had already adopted special and fantastic signs to represent certain substances.[2]

Dalton, who had clarified the conception of elementary substances and

---

[1] The specific volume is the volume occupied by a gram of any substance in the gaseous state at 0° and 760 mm. pressure. If, for example, one litre of air weighs 1·294 grm., a gram of air will have the specific volume of 773 c.c. The volume occupied by 1 grm. of hydrogen is 11,162 c.c., that is, 14·44 times more than that of air. The specific volume of oxygen is 699 c.c.

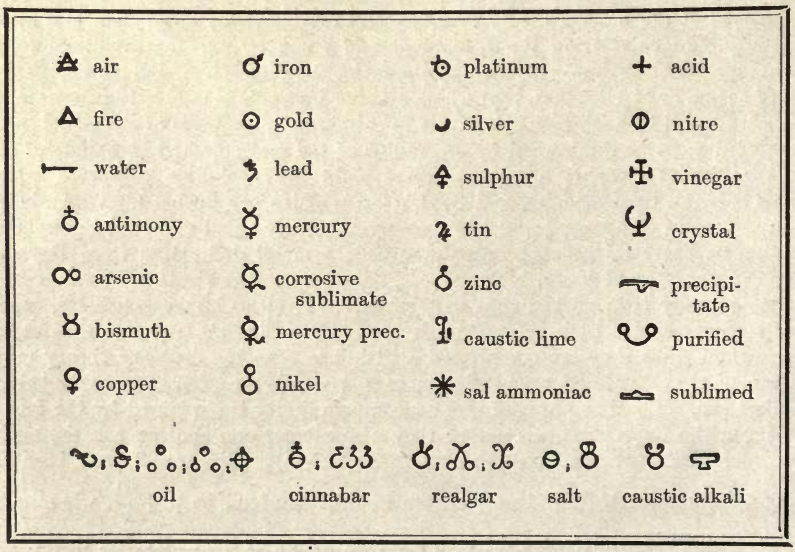


FIG. 14.

had given a concrete idea of the elements by means of his atomic hypothesis, imagining them to be formed of simple atoms, was, however, the first to propose the use of symbols to represent the atoms of the various elementary substances. The so-called non-metals, a special group of elements with non-metallic aspect, such as hydrogen, oxygen, chlorine, iodine, etc., were represented by conventional signs, for example, oxygen = ○, hydrogen ⊙, nitrogen ⦶, water ○⊙, ammonia ⊙⦶. For metals, on the other hand, he proposed to employ as a symbol the first letter of the corresponding Latin

TABLE OF ATOMIC WEIGHTS (1918)

Name of the Element	Symbol	Atomic weight		Name of the Element	Symbol	Atomic weight	
		O = 16	H = 1			O = 16	H = 1
Aluminium	Al	27·1	26·9	Molybdenum	Mo	96	95·3
Antimony	Sb	120·2	119·3	Neodymium	Nd	144·3	143·15
Argon	Ar	39·88	39·6	Neon	Ne	20·2	20·0
Arsenic	As	74·96	74·36	Nickel	Ni	58·68	58·3
Barium	Ba	137·37	136·27	Niton	Nt	222·4	221·42
Bismuth	Bi	208·0	206·34	Nitrogen	N	14·01	13·89
Boron	B	11	10·9	Osmium	Os	190·9	189·37
Bromine	Br	79·92	79·28	Oxygen	O	16	15·88
Cadmium	Cd	112·4	111·6	Palladium	Pd	106·7	105·85
Cæsium	Cs	132·81	131·75	Phosphorus	P	31·04	30·77
Calcium	Ca	40·07	39·75	Platinum	Pt	195·2	193·45
Carbon	C	12	11·91	Potassium	K	39·10	38·79
Cerium	Ce	140·25	139·2	Praseodymium	Pr	140·9	139·4
Chlorine	Cl	35·46	35·17	Radium	Ra	226·0	224·6
Chromium	Cr	52	51·58	Rhodium	Rh	102·9	102·08
Cobalt	Co	58·97	58·50	Rubidium	Rb	85·45	84·77
Columbium	Nb	93·1	92·75	Ruthenium	Ru	101·7	100·9
Copper	Cu	63·57	63·06	Samarium	Sa	150·4	149·2
Dyprosium	Dy	162·5	161·21	Scandium	Sc	44·1	43·8
Erbium	Er	167·7	166·07	Selenium	Se	79·2	78·6
Europium	Eu	152·0	150·79	Silicon	Si	28·3	28·07
Fluorine	F	19	18·9	Silver	Ag	107·88	107·02
Gadolinium	Gd	157·3	156·05	Sodium	Na	23	22·81
Gallium	Ga	69·9	69·34	Strontium	Sr	87·63	86·94
Germanium	Ge	72·5	71·9	Sulphur	S	32·06	31·81
Glucinum	Be	9·1	9·03	Tantalum	Ta	181·5	179·56
Gold	Au	197·2	195·7	Tellurium	Te	127·5	126·48
Helium	He	4·00	3·96	Terbium	Tb	159·2	157·93
Holmium	Ho	163·5	162·2	Thallium	Tl	204	202·38
Hydrogen	H	1·008	1	Thorium	Th	232·4	230·57
Indium	In	114·8	113·88	Thulium	Tu	168·5	166·16
Iodine	I	126·92	125·9	Tin	Sn	118·7	118·1
Iridium	Ir	193·1	191·5	Titanium	Ti	48·1	47·7
Iron	Fe	55·84	55·5	Tungsten	W	184	182·6
Krypton	Kr	82·92	82·26	Uranium	U	238·2	236·7
Lanthanum	La	139	137·9	Vanadium	V	51·0	50·8
Lead	Pb	207·2	205·45	Xenon	Xe	130·2	129·66
Lithium	Li	6·94	6·88	Ytterbium	Yb	173·5	170·63
Lutecium	Lu	175·0	171·5	Yttrium	Y	88·7	88·3
Magnesium	Mg	24·32	24·15	Zinc	Zn	65·37	64·85
Manganese	Mn	54·93	54·49	Zirconium	Zr	90·6	89·9
Mercury	Hg	200·6	198·5				

name, for example, Hg for mercury, from the Latin *Hydrargirium;* Fe (*ferrum*) for iron, etc.

Berzelius, who studied numerous substances and discovered new elements, confirming all the conclusions of Dalton's hypothesis, proposed a little later (1813) to represent also the non-metals by the first letters of their Latin names. It is this nomenclature which has survived until to-day, and is universally accepted. Dalton wrote the stoichiometric value (combining weight or equivalent) at the side of the symbol, taking hydrogen as unity. Later on Berzelius proposed to take oxygen as unity, but all the chemists very soon returned to the hydrogen unit, which persisted until a few years ago. To-day the atomic weights of the elements are referred to oxygen, which is taken as equal to 16, because it is easier to prepare very pure oxygen than very pure hydrogen, and also because the atomic weights of the other elements are thus obtained more exactly. On the previous page we give a table of the symbols of all the elements with atomic weights referred both to hydrogen = 1 and to oxygen = 16.

CHEMICAL FORMULÆ. By means of symbols we are also able to indicate very simply and clearly the molecules of various substances and of the elements themselves, the number of atoms contained in the molecules being indicated. Thus, for example, the molecule of hydrogen, which is formed of two atoms, is represented by the symbol H_2, the molecule of oxygen by O_2, that of chlorine by Cl_2, etc.; that is, the symbol is written and a number which indicates how many atoms enter into the molecule is written to the right of it, either below, as proposed by Poggendorf, or above, as proposed by Berzelius (and still used by some).

The molecular formula of hydrochloric acid is HCl, that of water, which contains two atoms of hydrogen and one of oxygen, H_2O, and that of ammonia, NH_3. These formulæ show that one volume of hydrogen gas combines with one volume of chlorine to give hydrochloric acid, and that two volumes of hydrogen gas are combined with one volume of oxygen gas to give water, as was demonstrated by Gay-Lussac, etc.

If the symbols constitute the chemical alphabet, the formulæ must be considered as the words of the chemical language. It is a language formed by equations which express the various reactions occurring between different molecules, thus forming a kind of chemical algebra.

The molecular formulæ show also the molecular weight of each chemical element or compound; thus, the molecular formula of hydrogen, H_2, shows that the molecular weight is 2 ($H = 1$); that of oxygen shows that the molecular weight is 32 or twice the atomic weight of oxygen (16×2); from the molecular formula of hydrochloric acid the molecular weight is seen to be 36·5, *i. e.*, the weight of an atom of hydrogen (1) + the weight of an atom of chlorine (35·5); consequently 36·5 kilos of pure hydrochloric acid gas contain 35·5 kilos of chlorine and 1 kilo of hydrogen. In 18 kilos of water, 2 kilos of hydrogen and 16 kilos of oxygen are contained, the molecular weight of water being 18.

The formula of any substance gives its molecular weight, and thence the percentage composition can be deduced in a simple manner. For water, for example, we have:

$$\begin{array}{lll} H_2 = 2 & 18\,(H_2O) : 2\,(H_2) = 100 : x & x = 11{\cdot}12\% \text{ of H} \\ O = 16 & 18\,(H_2O) : 16\,(O) = 100 : x' & x' = 88{\cdot}88\% \text{ of O} \\ \overline{\text{molecular weight } 18} & & \overline{\text{per 100 parts of water}} \end{array}$$

Thus electrolytic decomposition of 100 kg. of water (this process is now carried out on an industrial scale) yields 88·88 kg. of oxygen and 11·12 kg. of hydrogen.

In the case of sulphuric acid, which has the formula H_2SO_4, we have :

$$\begin{array}{lll} \left\{\begin{array}{l} H_2 = 2 \\ S = 32 \\ O_4 = 64 \end{array}\right. & \left\{\begin{array}{l} 98 : 2\,(H_2) = 100 : x \\ 98 : 32\,(S) = 100 : x' \\ 98 : 64\,(O_4) = 100 : x'' \end{array}\right. & \begin{array}{l} x = 2{\cdot}04\% \text{ of hydrogen} \\ x' = 32{\cdot}65\% \text{ of sulphur} \\ x'' = 65{\cdot}31\% \text{ of oxygen} \end{array} \\ \hline \text{molecular weight } 98 & & \text{per } 100 \text{ of sulphuric acid} \end{array}$$

We are thus able to deduce that in a sulphuric acid works, if there is no loss, 100 kilos of sulphuric acid should be obtained per 32·65 kilos of sulphur employed.

From the percentage composition of a substance—which is determined by means of ordinary chemical analysis[1]—together with the determination of its vapour density or of some other magnitude leading to its molecular weight, its formula can be deduced.

If, for example, we wish to determine the formula of water, we commence by making a quantitative analysis (*see later*, chapter on Water), which allows us to ascertain the percentage composition : $H = 11{\cdot}12$ per cent., $O = 88{\cdot}8$ per cent. If we now determine the density of water vapour compared with that of air, we find that it is 0·626, and multiplication of this by 28·88 gives the molecular weight, which is $28{\cdot}88 \times 0{\cdot}626 = 18$. The amounts of oxygen and hydrogen in 18 parts of water (molecular weight) are then established by simple proportion, the percentage composition being taken into account :

$$\begin{array}{ll} 100 : 11{\cdot}12\,(H) = 18 : x & x = 2 \\ 100 : 88{\cdot}88\,(O) = 18 : x' & x' = 16 \end{array}$$

The quantities by weight of the individual elements contained in the molecule correspond with the atomic weights of these elements or, where several atoms are present, with multiples of these. Thus by dividing the values, x and x', by the atomic weights, we shall obtain the numbers of atoms of these elements contained in a molecule of water.

$$\begin{array}{r} 2 : \ 1 \text{ (atomic weight of H)} = 2 = H_2 \\ 16 : 16 \text{ (atomic weight of O)} = 1 = O \end{array}$$

The chemical formula of water is, therefore, H_2O. The formulæ of numerous other inorganic and organic substances are found in the same way.

This is the simplest method of calculating the formulæ of substances, but it cannot be employed when the molecular weight is not known. In this case the end is attained by means of indirect methods which are often employed in organic chemistry, for example, the formation of salts, other derivatives, etc.

DUALISTIC FORMULÆ. Lavoisier believed that when a base and an acid combine to form a salt they retain their original constitution in the new molecule. From this idea Lavoisier derived his system of dualistic formulæ for representing the molecules of salts. Thus, he wrote the formula of calcium carbonate as $CaO.CO_2$, because he supposed the components lime, CaO (base), and carbon dioxide, CO_2 (acid), to exist side by side within the molecule. Sulphuric acid was represented by the dualistic formula $SO_3.H_2O$, as it was supposed to contain the separate components SO_3 (sulphur trioxide) and H_2O (water).

In 1819 Berzelius, in his studies on the intimate nature of chemical compounds, based on the conceptions of Lavoisier and the work of Davy, enunciated an electrolytic theory of dualistic formulæ, according to which all compound substances were regarded as composed of two parts with different electric charges, negative and positive, namely, the acid

---

[1] By *analysis* in general is understood the operation of splitting a given substance into any or all of its components in order to determine its composition, whilst by synthesis is understood that chemical process by means of which a complex substance is obtained, starting from other simple substances. Thus analysis is the demolition, whilst synthesis is the reconstruction, of one or more chemical structures. Synthesis is often used in order to test the exactitude of analysis, and *vice versa*.

residue—negative—(oxy-acids were alone well known at that time, but not the halogen acids) and the basic residue—positive; for example:

$$\overset{+}{\overparen{\mathrm{BaO}}} \,.\, \overset{-}{\overparen{\mathrm{SO_3}}} \qquad\qquad \overset{+}{\overparen{\mathrm{ZnO}}} \,.\, \overset{-}{\overparen{\mathrm{CO_2}}}, \text{ etc.}$$

Barium sulphate   Zinc carbonate

By electrolytic decomposition of these salts, the components of the molecule were supposed to separate, and confirmation of this idea was sought in the appearance of the two substances at the two poles of a cell (voltameter). The classic experiment of this epoch was the electrolytic decomposition of a solution of sodium sulphate ($SO_3.Na_2O$).

At the positive pole, where the acid residue should have been formed, litmus solution did actually become red, and at the negative pole, where the basic residue should have been obtained, the litmus was coloured blue. Daniell had, however, already perceived that the results which are apparently obtained by electrolysis really occur in another manner, and that it is not sodium oxide which separates at the negative pole, as had always been supposed, but metallic sodium; the latter combines with the water of the solution at the instant of its formation and thus forms the base which colours the litmus blue. If mercury is taken as the negative pole, this at once fixes a part of the metallic sodium as it is liberated, giving sodium amalgam; it is thus shown that, in the electrolytic decomposition of sodium sulphate, metallic sodium and not sodium oxide is obtained at the negative pole. It was in this very manner that Davy discovered and isolated sodium and potassium.

It was observed, on the other hand, that a gas was developed at the positive pole, this gas being identified as oxygen. Thus on electrolysing copper sulphate, copper oxide (CuO) should be obtained at the negative pole, and the sulphuric acid residue (SO_3) at the positive pole, according to the dualistic theory; actually, however, metallic copper was obtained at the negative pole and oxygen was developed at the positive pole, sulphuric acid being also formed.

Liebig, who at first opposed the unitary formula of Davy, finished by abandoning the dualistic theory of Berzelius, which had also been shaken to its foundations by the important work of Dumas, Laurent, and Gerhardt.

Salts are to-day considered to be composed of a metallic (positive) residue and of an acid (negative) residue; the latter may be either oxygenated or non-oxygenated (in the case of the halogen salts, such as sodium chloride, etc.). According to this conception, then, the fact that metallic copper separates at the negative pole and oxygen at the positive pole in the case of copper sulphate ($CuSO_4$) is explained, because the acid residue of copper sulphate, namely, SO_4, is unstable and at once decomposes, giving oxygen and sulphur trioxide (SO_3), which yields sulphuric acid with water. The error committed by Berzelius was that he did not take into account the oxygen which is developed, but only the acid reaction.

The theory of Berzelius was completely abandoned many years ago, the results obtained when the residues of the non-oxygenated halogen acids and of the polybasic acids were studied, being inexplicable by means of the dualistic theory.

VALENCY

By studying the various compounds represented by chemical formulæ more closely and intimately, we are able to indicate the manner in which the atoms are united with one another in the molecule, and to explain why, in the case of chemical reactions, certain atoms are constantly found united with one or more atoms of other elements. Given that there is an attraction or affinity between atoms of various kinds, it is interesting to know in what manner they saturate one another reciprocally.

Glauber in the Middle Ages, and Wenzel and Richter later, determined the proportions of saturation of a certain quantity of an acid by various quantities of different bases, or *vice versa*.

In 1811, Berzelius clarified this conception by finding a simple and constant relation between the oxygen of a base and that of an acid constituting a salt. It was found that a molecule of potassium nitrate contained a quantity of nitric acid corresponding with one molecule of this acid, whilst a molecule of ferric nitrate contained a quantity of nitric acid corresponding with three molecules of the acid, that is to say, that potassium oxide—which is the base combined with the nitric acid in potassium nitrate, KNO_3—represents a mono-acid base, whilst oxide of iron in ferric nitrate, $Fe(NO_3)_3$, is a tri-acid base. Numerous bases are known which have various valencies or powers of saturation for this acid.

In 1835 Graham demonstrated the polybasicity of phosphoric acid, and in 1845–1850 Kolbe, by means of his classic studies on the radicals of organic compounds, prepared the ground for Frankland and his fertile and brilliant conception of the theory of valency (1853), which was extended to organic compounds by Kekulé and subsequently to inorganic compounds and to all the elements. Still later, Wurtz, by a notable series of experimental researches, showed that a reciprocal power of saturation also exists between elementary substances, thus throwing light on the relation between the theory of variable valency and Dalton's law of multiple proportions.

The *constant* valency of the elements generally found confirmation in organic compounds, whilst various examples of *variable* valency were found among inorganic compounds, and thus the conception of valency grew and acquired a wider horizon.

We may easily grasp the simple conception of valency if we arrange a certain number of substances according to their chemical compositions in a small table, according to a definite plan :

HCl	$HgCl_2$	PCl_3	CCl_4	$NbCl_5$
HBr	OCl_2	$AsCl_3$	$SiCl_4$	$TaCl_5$
HI	$BaCl_2$	$SbCl_3$	$SnCl_4$	
HF	$ZnCl_2$	$BiCl_3$	CH_4	
KCl	$CuCl_2$	BCl_3	SiH_4	
$NaCl$	SH_2	NH_3		
$AgCl$	OH_2	AsH_3		

The first vertical column contains the formulæ of four halogen acids, the molecules of which are all formed of one atom of hydrogen, combined or saturated with one atom of Cl, Br, I, or F, so that one may say of these elements that they are monovalent with respect to hydrogen. We next find in the same column three salts, the molecules of which contain one atom of Cl, which is monovalent (that is, has the power of saturating one atom of H) and is now combined with one atom of K, Na, or Ag. Thus we may also consider K, Na, and Ag as monovalent elements, because one atom of these saturates a single atom of chlorine, which in turn saturates a single atom of hydrogen. In the second column we find elements the atoms of which are saturated by two atoms of monovalent chlorine; thus, these elements, Hg, O, Ba, Zn, and S, are divalent, that is, have a power of saturation corresponding with two atoms of chlorine or with two atoms of hydrogen.

In the third column we have trivalent, in the fourth column tetravalent, and in the fifth column pentavalent, elements.

Elements which have the same capacity for saturation are able to substitute one another reciprocally in their various combinations, giving products of analogous composition. Thus, we can carry out practically the following series of reactions and successive substitutions :

(*a*) $2NO_3H + Ag_2 = H_2 + 2NO_3Ag$
(*b*) $2NO_3Ag + Hg = Ag_2 + (NO_3)_2Hg$
(*c*) $(NO_3)_2Hg + Cu = Hg + (NO_3)_2Cu$
(*d*) $(NO_3)_2Cu + Zn = Cu + (NO_3)_2Zn$
(*e*) $(NO_3)_2Mg + Na_2O = MgO + 2NO_3Na$

As we see here, two atoms of monovalent silver replace two atoms of H (*a*), and are in turn replaced by one atom of divalent mercury (*b*), and this by one atom of divalent copper (*c*); the copper is replaced by one atom of divalent zinc (*d*). One atom of divalent magnesium replaces two atoms of monovalent sodium (*e*), so that this atom has the power of saturation by two atoms of H and can also replace two atoms which have the capacity for saturating one atom of H, for example, Hg corresponds with Ag_2.

Hence elements which have the same *capacity for saturation* by H have also the same *capacity of combination*, that is, in a given chemical compound they may substitute or replace one another reciprocally, always giving rise to *saturated* molecules which no longer have any disposable affinity enabling them to combine with further quantities of the element they contain. We may thus define the capacity of combination also as the *capacity for saturation* or the VALENCY of the elements, and this is actually expressed and indicated by small indices or by Roman numerals which are placed above the symbol of the element on the right.

Monovalent elements then are those which have the capacity for being saturated by a single atom of H, *e. g.*, Cl', I', Br', F', etc.

Divalent elements are capable of saturation by two atoms of H or other monovalent element, for example, Cu'', Ba'', Zn'', S'', O'', etc.

Trivalent elements saturate three atoms of H or three monovalent atoms or one monovalent and one divalent atom, for example, N''', Sb''', As'''.

Tetravalent elements saturate 4 H or four other monovalent atoms, or two divalent atoms, etc., for example, C^{iv}, Si^{iv}.

The same applies to the pentavalent elements, columbium and tantalum, Nb^{v}, Ta^{v}.

It must, however, be remembered that valency is a property entirely distinct and different from chemical affinity. Thus, hydrogen and fluorine, which are only monovalent, have an extraordinary reciprocal chemical affinity, whilst nitrogen, which is trivalent, has very little affinity for hydrogen or other elements.

The valency of an element is measured by the number of atoms of hydrogen or of monovalent elements which it can saturate, whilst, on the other hand, affinity is measured by the quantity of energy which the substance develops during combination. There is no connection between valency and affinity, just as there is no connection between the height or the weight of a person and his muscular or intellectual power. We shall later explain more rationally the conceptions of affinity and valency (*see* Valency of the Ions and Affinity).[1]

We have now studied and discussed the significance of the equivalents, that is, of the stoichiometric or combining weights of the elements, referred to unit weight of hydrogen, these values being deduced from percentage compositions.

We know, in fact, that on analysing water we find it to consist of 88·88 per cent. of oxygen and 11·12 per cent. of hydrogen; that is to say, that 1 of H corresponds with 8 of oxygen. This figure 8 is the stoichiometric value or equivalent of oxygen, that is, the quantity which combines with 1 of H.

In the same manner, on analysing ammonia we find 82 per cent. N and 18 per cent. H; the stoichiometric value or equivalent of nitrogen is thus equal to 4·67, which is the quantity which corresponds with 1 of H.

---

[1] The conception of valency has now been further widened, and for each element the maximum valency should be considered in explaining its behaviour in cases where the valency appears to be diminished. The formation of certain compounds is to-day regarded as due to the existence of *secondary valencies, counter-valencies, residual valencies, supplementary valencies*, etc.

By *principal valencies* are meant those of the electrons composing the atoms of the elements, and by *secondary valencies* those which are saturated in individual molecules and which determine a selective and, hence, variable affinity with respect to different atoms.

For every element Abegg assumes valencies and counter-valencies, the sum of which is 8 in all cases. Ramsay supposes that every positive elementary atom is united to a negative electron, whilst Stark reduces valency to a purely electrical affinity, which does not, however, explain the selective affinities of different elements.

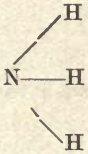
If now we compare these equivalents of oxygen and of nitrogen with their relative atomic weights, we have:

	O	N
Equivalent	8	4·67
Atomic weight	16	14

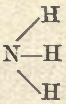
and we at once see that a simple relationship exists between the equivalents and the atomic weights. For oxygen the atomic weight is twice the equivalent, while for nitrogen it is three times the equivalent, and we have already found that oxygen is divalent and nitrogen trivalent. Thus the valency is a function of the combining weights or stoichiometric values. The latter represent, as it were, fractions of atoms corresponding in each case with one valency or with one atom of hydrogen. Thus the valency, or capacity for saturation, of the elements is easily found or determined when the atomic weight—which can be determined in various ways—and the stoichiometric value—which may easily be found by analysing a given compound—are known; division of the atomic weight by the equivalent then gives the valency.

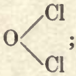
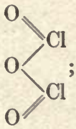
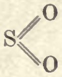
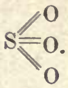
Formulæ in which the manner of distribution and combination of the atoms in each molecule are shown, and in which the valencies are represented by small lines, are called *constitutional formulæ*, while those giving merely the numbers of the atoms of each element composing the molecule are called *empirical formulæ*.

Thus the empirical formula of ammonia is NH_3, and nitrogen, being trivalent, its constitutional formula will be:



or more simply

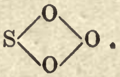


The valency of a given element is not, however, a constant property, but varies with the substance upon which it is exerted. For example, chlorine is always monovalent with regard to hydrogen, whilst with regard to oxygen it may be di-, tri-, tetra-, penta-, and heptavalent: HCl;  ;  ; similarly sulphur is divalent with respect to hydrogen, but tetravalent and also hexavalent with respect to oxygen  ; .

The valency of metals with respect to oxygen sometimes varies with variation of the temperature, and if this is high, we have the minimum valency, and if low, the maximum valency, that is, the compound of maximum oxidation. If the temperature is very high the affinity for oxygen may be altogether overcome by the so-called tension of the oxygen; the free metal is then formed, as can be seen in the following table:

CuO yields Cu_2O at 1110°, and Cu at 1800°.
Tl_2O_3 yields Tl_2O at 875°, and Tl at 1865°.
PbO_2 yields Pb_3O_4 at 390°, PbO at 615°, and Pb at 2240°.
Sb_2O_5 yields SbO_2 at 450°, Sb_2O_3 at 1060°, and Sb at 2490°.
MnO_2 yields Mn_2O_3 at 570°, Mn_3O_4 at 1090°, MnO at 2500°, and Mn at 4050°.
Fe_2O_3 yields Fe_3O_4 at 1970°, and Fe at 3025°.
Co_2O_3 yields CoO at 895°, and Co at 2860°.
PdO_2 yields PdO at 180°, and Pd at 875°.

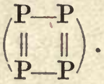
Until a few years ago, some chemists—and there are a few even now—did not accept the conception of variable valency of the elements and in the case of abnormal compounds supposed that there were either free valencies, as in carbon monoxide, $C \equiv O$:, or a reciprocal saturation between elements of the same nature, linking them together with one another, as in chlorine oxide : $Cl—O—O—O—Cl$, or sulphur trioxide



To-day, however, numerous organic and inorganic compounds are known which show that when an element appears to be saturated with respect to its ordinary valencies, it will always possess affinities for other elements or molecules, so that one is forced to admit another form of valency which is regularly exercised under certain conditions.

There are also various thermochemical data and other observations, such as the behaviour of the ions (to be studied later) which are not in accord with the conception of constant valency.

Now that we are acquainted with valency and its signification, we are also able to explain why the elements themselves are generally not composed of atoms in the free state, but why these are always grouped into molecules. In the latter the valencies or affinities of the atoms remain saturated and the molecules may be represented thus : $(H - H)$, $(S = S)$, $(N \equiv N)$, $(Cl - Cl)$; phosphorus is trivalent, but we know from its vapour density that its molecule is composed of four atoms and may be represented thus :



MONATOMIC MOLECULES. We already know how the molecular weight of a substance is found from its vapour density, and we have also seen that most simple substances are formed of diatomic molecules.

When, however, the vapour densities of certain simple substances, *e. g.*, mercury, zinc, and certain of the new gaseous elements, such as argon, etc., are determined it is found that the molecules of these substances are formed, not of two atoms, but of a single atom only; these substances are therefore composed of free atoms, that is, of monatomic molecules.

Obviously these substances cannot be proved to be monatomic by direct deduction from the vapour density, because this determines merely the relative weight of the free particles of a gas or vapour, compared with that of the free (diatomic) particles of hydrogen, without indicating whether the former are composed of 1, 2, 3, or more atoms. If mercury, with a vapour density of 200, consisted of diatomic molecules, its atomic weight would be $\frac{200}{2}$, that is, 100, but the study of other gaseous mercury derivatives always gives an atomic weight of 200 for mercury, that is, one which is equal to the molecular weight indicated by the vapour density; we must therefore assume that mercury particles in the state of vapour are monatomic and that the value 200, derived from the vapour density compared with hydrogen, indicates directly the atomic weight of mercury. The same remarks apply to the vapours of zinc and of all other metals.

The presence of monatomic molecules cannot be confirmed (by ordinary means) in the case of simple substances which do not enter into chemical combinations; in such cases other indirect methods are employed. Thus, the size of the molecules of certain rare elementary gases of the atmosphere, viz., argon, helium, xenon, neon, and krypton, has been determined by means of their specific heats at constant pressure and at constant volume. It was not found possible to obtain any compounds of these substances, and it was therefore not known with certainty whether their density compared with that of hydrogen indicated monatomic or diatomic molecules, and, therefore, whether the atomic weight was equal to, or one-half of, that indicated by the density of the gas. Lord

Rayleigh has recently been able to show that these gases are composed of monatomic molecules by means of investigations of their specific heats (as we shall explain below) and thus demonstrated that the molecular weights of these gases are identical with their atomic weights.

THERMAL CAPACITY AND SPECIFIC HEAT OF GASES. PRINCIPLES OF THERMODYNAMICS

If a gas is heated its temperature is raised. The ratio between the heat which is added and the rise of temperature (expressed in degrees Centigrade) is called the *thermal capacity* of the gas, and varies with the nature of the gas, with the temperature, and with the pressure, whereas in the case of liquids and solids, pressure has virtually no influence on this property. A *calorie* is the quantity of heat required to raise 1 grm. of water from 0° to 1°.

The expression thermal capacity arose in the epoch during which it was still believed that heat was composed of some kind of material substance (Newton).

The term *specific heat* (c) denotes the thermal capacity of unit weight of a gas, that is, the amount of heat necessary to raise the temperature of 1 grm. of the substance by one degree, while the thermal capacity of a gram-molecule of the gas is called the *molecular heat* (C). At high temperatures (such as 1000° or 2000°, or above) the specific heat of gases increases somewhat.

The specific heat of a gas may be determined at *constant pressure* (c_p) or at *constant volume* (c_v); the former value is always larger than the latter, and for molecular heats the difference is about two calories: $C_p - C_v = 2$ cals. (*see* Table below). These two calories represent the heat which is absorbed by the gas to supply the work done during dilatation, and we are thus able to calculate, from the difference between these specific heats, the amount of heat evolved when a gas decreases in volume, and also when it passes from the gaseous into the liquid or solid state (*see* p. 27).

We may deduce these results from the following considerations, which lead to the first law of thermodynamics, by means of which the equivalence between heat and mechanical work (*see also* p. 53) is established. The heat required to raise the temperature of 1 grm. of air (that is, 773 c.c.) by 1° at constant pressure is given by the specific heat c_p, which is 0·2375 cal.; the heat required to raise the temperature by the same amount at constant volume is given by the specific heat c_v, which is 0·1683 cal. The difference, viz., 0·0692 cal., indicates that portion of the heat which is converted into work, the latter being expressed by the product of the pressure p, and the increase of volume dv, that is, by $p\,.\,dv$. Since the volume of any gas, according to the law of Gay-Lussac, increases by $\frac{1}{273}$ for each degree rise of temperature, dv will in this case be $\frac{773}{273} = 2{\cdot}83$ c.c., and the pressure exerted by the atmosphere on each sq. cm. of surface being 1033·3 grms., we have: $p\,.\,dv = 1033{\cdot}3 \times 2{\cdot}83 = 2924{\cdot}24$ grm.-cms., which represents the mechanical equivalent of the quantity of heat, $c_p - c_v$, that is, 0·0692 cal.

We are now able to deduce the mechanical equivalent of heat by comparing the heat absorbed with the resulting work. We thus find that $\frac{2924{\cdot}24}{0{\cdot}0692} = 42{,}260$ gram-centimetres (or ergs, *i. e.*, absolute units of energy)[1] represent the work equivalent to a small calorie ($0{\cdot}0692$ cal. : $2924{\cdot}24 = 1 : x$; $x = 42{,}260$);[2] and for a large calorie (that

---

[1] *Translator's Note.*—An error has here crept into the original text. The erg, which is the absolute unit of energy on the C.G.S. system, is the work accomplished by a movement through 1 cm. against a resisting force of 1 dyne (*see* p. 27).

[2] The absolutely correct value for this is 42,720 (*see* p.27); it is the quantity of energy expressed in absolute (?) (*see* Translator's Note above) units, each of which suffices to raise 1 grm. of matter against gravity through a distance of 1 cm. The equivalent of the large calorie (1000 small calories) is 42,720,000 grm.-cms., or 427·2 kilogram-metres (each of which suffices to raise 1000 grms. through a height of 100 cms. against the action of gravity); this is the mechanical equivalent of the large calorie, which is simply called the mechanical equivalent of heat. The difference, $C_p - C_v$, in correct values is 1·985 cals.

is, for 1000 small calories) we have 422·6 kilogram-metres, which is the value of the mechanical equivalent of heat (*see* Note).

On introducing this equivalent (A) in order to calculate the work produced we have: $A(C_p - C_v) = p \, . \, dv = p(v_2 - v_1) = pv$, where v_1 and v_2 are the volumes of the gas before and after heating, and v the difference between them. From the general gas equation, taking a temperature difference of 1 degree, so that $(T_2 - T_1) = 1$, we obtain $A(C_p - C_v) = R$ (T being equal to 1), and it is then possible also to deduce in this manner the value of the gas constant, R, which must always be referred to a gram-molecule of the gaseous substance. We already know that the value of R is 84,780 (*see* p. 27), and if we wish to express this in thermal units by giving to C_p and C_v the values of the molecular heats we have: $C_p - C_v = \frac{R}{A}$, that is, $\frac{84780}{42260}$ = about 2 calories, if A denotes the thermal equivalent of a small calorie expressed in gram-centimetres. *The difference between the specific heats at constant pressure and at constant volume is thus equal to about* 2 *calories* for each gram-molecule.

It has also been found that the ratio between the specific heats at constant pressure and at constant volume $\left(\frac{C_p}{C_v}\right)$ diminishes with increase in the number of atoms in the molecule.

Gaseous substance	Specific heat[1]		Molecular heat (molecule of hydrogen = 2)		Difference $C_p - C_v$	Ratio $\frac{C_p}{C_v}$	Number of atoms in the molecule
	at constant pressure C_p	at constant volume C_v	at constant pressure $= C_p$	at constant volume $= C_v$			
Oxygen .	O_2 = 0·2175	0·1551	6·96	4·96	2	1·40	2
Nitrogen .	N_2 = 0·2438	0·1727	6·83	4·83	2	1·41	2
Hydrogen .	H_2 = 3·4090	2·411	6·82	4·82	2	1·41	2
Carbon dioxide	CO_2 = 0·2169	0·172	9·55	7·55	2	1·33	3
Ammonia .	NH_3 = 0·5284	0·391	8·64	6·64	2	1·37	4
Methane .	CH_4 = 0·5929	0·468	9·49	7·49	2	1·27	5
Ethyl ether .	$C_4H_{10}O$ = 0·4797	0·453	35·50	33·50	2	1·06	15

As has already been stated, mercury in the state of vapour contains monatomic molecules, and the relation between its molecular heats, $\frac{C_p}{C_v} = 1·666$. Now by means of

---

[1] For various practical purposes the specific heats of gases and vapours at constant pressure (water = 1) are often required:

Substance	Temperature of experiment	Specific heat	Substance	Temperature of experiment	Specific heat
Air . . .	from —100° to + 200°	0·2374	Carbon dioxide .	10°–214°	0·2169
,, at 20 atm. .	at — 120°	0·4700	Nitric oxide . .	13°–170°	0·2317
,, ,, 70 ,, .	at — 120°	0·7770	Nitrogen peroxide .	27°– 67°	1·625
Oxygen . .	from 10° to 200°	0·2175		27°–150°	1·115
,, liquid .	— 200° to — 183°	0·3470		27°–280°	0·650
Hydrogen . .	— 30° to + 200°	3·410	Ammonia . .	20°–200°	0·52
,, at 30 atm.	—	3·7882	Sulphur dioxide .	16°–200°	0·1544
Nitrogen . .	0°–200°	0·2438	Hydrogen sulphide.	20°–200°	0·2451
,, liquid .	—	0·430	Carbon disulphide .	86°–190°	0·1596
Argon . . .	20°– 90°	0·1233	Water vapour .	100°	0·421
Chlorine . .	10°–202°	0·1241	,, ,, .	180°	0·510
Bromine . .	20°–388°	0·0554	Methane . .	18°–208°	0·5930
Iodine . .	206°–377°	0·0336	Ethyl alcohol	108°–220°	0·4534
Hydrogen chloride	10°–200°	0·190	Methyl ,, . .	101°–223°	0·4580
,, bromide.	10°–100°	0·0820	Ethyl ether . .	27°–190°	0·4618
,, iodide .	20°–100°	0·0550	Benzene, C_6H_6 .	116°–218°	0·3754
Carbon monoxide .	20°–200°	0·2425	Acetone . .	129°–233°	0·4125
,, dioxide .	15°–100°	0·2025	Chloroform . .	28°–189°	0·1489

the kinetic theory of gases, one is able to demonstrate mathematically that for free atoms, or monatomic molecules, the relation $\frac{C_p}{C_v}$ must be 1·667 (*see* below). The fact that mercury vapour consists of monatomic molecules is thus confirmed. The ratio $\frac{C_p}{C_v}$ varies between 1 for very large molecules, that is, such as contain many atoms, and 1·4 for diatomic molecules, whilst for monatomic molecules it approaches 1·667.

The determination of the ratio between the specific heats of gases at constant pressure and at constant volume has led, as has already been stated, to the demonstration that the molecules of the gases, argon, helium, krypton, xenon, and neon are formed even at ordinary temperatures of monatomic molecules, and since these gases are very indifferent and give no combinations with other elements, it was impossible to control their molecular weights by the densities. The densities of these gases represent nothing but relative values, that is, maximum limits, and show that the free particles of these gases have a given weight relatively to those of hydrogen; this does not, however, decide whether such weight represents diatomic molecules or free atoms. Only by means of the ratio of the specific heats $\frac{C_p}{C_v} = 1·667$ was Lord Rayleigh able to demonstrate that the molecules were monatomic.

By the kinetic theory of gases we are also able to explain the relation which exists between the specific heats of a gas and the number of atoms contained in its molecule.

We know (*see* p. 7) that on heating a gas its *internal energy* is increased by an amount, dU, resulting from an increase of its *molecular kinetic energy*, dU_m, or *internal kinetic energy*, or energy of motion due to the rise of temperature and to the increase of the *internal potential energy* (or energy of position, *see* p. 4). In order to determine the latter, that is, the quantity of energy necessary to alter the positions of the atoms in the molecule of the gas, we require to know the difference, $dU - dU_m$. In the case of the monatomic molecules this difference becomes equal to zero, because no part of the energy, dU, is consumed by increasing the distance between the atoms of the molecule, it being wholly employed in increasing the molecular kinetic energy, that is, in increasing the temperature, so that $dU = dU_m$ or $\frac{dU_m}{dU} = 1$.

If we wish to express the total increase of energy, dU, as a function of the temperature for a mass of gas, M, and for an increase of temperature, dT, then for the specific heat at constant volume, C_v, we shall have the equation:

$$dU = M \, . \, C_v \, . \, dT.$$

The equation of Clausius and Krönig, deduced from the kinetic theory of gases (p. 37) for the mass, M $(= n \, . \, m)$, then becomes $\frac{3}{2} MRT = \frac{Mc^2}{2}$. The increase in the molecular kinetic energy, $\frac{Mc^2}{2}$, which we have expressed by dU_m, thus corresponds with the rise of temperature, dT, and we arrive at the equation, $dU_m = \frac{3}{2} MRdT$. But we are able to replace the gas constant, R, by the corresponding expression in thermal units resulting from the difference, $C_p - C_v$ (*see above*), and we thus have: $dU_m = \frac{3}{2} M (C_p - C_v) \, dT$. Dividing this increase of the molecular kinetic energy by the total increase of internal energy, $dU = MC_v dT$, we obtain: $\frac{dU_m}{dU} = \frac{3}{2} \frac{C_p - C_v}{C_v}$, and in the case of monatomic molecules, $\frac{3}{2} \cdot \frac{C_p - C_v}{C} = 1$, that is, $\frac{C_p}{C_v} = \frac{5}{3} = 1·667$.

We have thus shown that for monatomic substances, the ratio between the specific heats $\frac{C_p}{C_v}$ must either equal or approximate to 1·667, and will always depart from this value in the direction of unity more and more as the molecules become more complicated by increase in the number of their atoms. It is precisely by this method that

Rayleigh has shown that the new gases of the atmosphere, argon, helium, etc., are composed of monatomic molecules.

SECOND LAW OF THERMODYNAMICS. This was deduced theoretically by Carnot (1824),[1] and established the amount of work which can be obtained from a given quantity of heat. We may explain this principle graphically by supposing that a given quantity of gas enclosed in an ideal cylinder provided with a piston and able to receive or emit heat only through its base, is subjected to a closed cycle of transformations. If the gas, the conditions of temperature and pressure of which, and therefore also its absolute temperature, T_1, are determined by the point A with respect to the two orthogonal axes of pressure, OP, and volume, OV (Fig. 15), is placed over an inexhaustible source of heat, it tends to expand up to the point B, and as the heat-supply prevents any cooling (in consequence of the dilatation), it is maintained at a constant temperature, the change being thus an isothermal one; the absorbed heat may be denoted by Q_1, while the work done during expansion is represented by the surface $a\,b\,B\,A$. If the gas were to expand without being in contact with the source of heat, it would be cooled down to T_2, because the expansion occurs at the expense of the internal kinetic energy. This cooling is equivalent to the mechanical work done during expansion, and in this case we have an adiabatic transformation, there being no exchange of heat with the external medium.

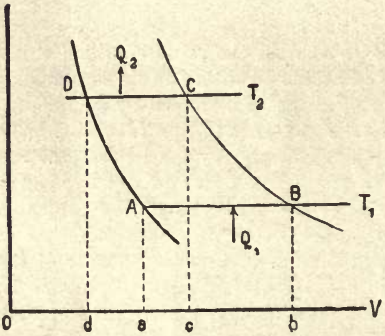


FIG. 15.

Now on compressing the gas adiabatically (that is, without addition or abstraction of heat) down to the volume c, we increase not only the pressure but also the temperature (to T_2). On then compressing the gas isothermally (that is, on placing the gas over an ideal refrigerator which abstracts the heat developed during compression) from the volume c to the volume d, the quantity of heat abstracted will be Q_2. On allowing the gas finally to expand adiabatically up to the original volume a, it will then acquire the original pressure and temperature, T_1, at the point of departure, A. On recommencing the experiment one can repeat the same closed cycle of transformations, which always bring the gas back to the original conditions of volume, temperature, and pressure, by passing alternately through two adiabatic and two isothermal transformations.

The surface $A\,B\,C\,D$ enclosed in the cycle represents the total useful work produced by the total quantity of heat, $Q_1 - Q_2$. A calculation which we will not reproduce here leads to the important equation:

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1},$$

---

[1] Nicolas Léonard Sadi Carnot, the son of Lazarus Carnot, was born on the 1st of June, 1796, at Paris and died there on Aug. 24th, 1832. His thermodynamical principle was enunciated in the work entitled "La puissance motrice du feu et les machines propres à développer cette puissance" (Paris, 1824), but it remained forgotten until, more than half a century later, Kelvin and Clausius worked at it.

Carnot had shown that only a small part (15 per cent. at the most) of the total heat supplied to a steam-engine can be transformed into work, and that this depended, not merely on mechanical imperfections in the engine—which could be improved—but on intrinsic and immutable conditions. Whereas the first law of thermodynamics states that the total energy of any system is invariable, the second law tells us that the utilisable energy undergoes diminution. Energy of motion may be converted completely into heat, but heat is only partially transformable into motion; the rest of the heat is dispersed partly by radiation into the surrounding medium and partly in the maintenance of the mechanism itself at a temperature above that of this medium (*see* p. 7). Without temperature differences in the universe no phenomena could take place, but these differences tend slowly and gradually to diminish, and when they disappear entirely, every vital and other phenomenon will cease. This degradation of energy is very slow, owing to the reversibility of so many phenomena, so that the death of the universe is still far distant—calculations indicate millions of centuries. The discovery of the radioactive substances (*see also* Radium) has shown that the calculated results are lower than the true ones, owing to the enormous quantities of energy continually generated when the chemical elements enter into existence.

which says that the ratio between the respective quantities of heat abstracted from and supplied to the gas is equal to the ratio between the respective absolute temperatures of the refrigerator and of the source of heat.

The ratio between the quantities of heat transformed into work and the quantity furnished to the gas, which is given by Carnot's cycle, may be deduced by writing the last equation thus:

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \text{ or } \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

Thus the efficiency depends on the temperature interval, $T_1 - T_2$, and it is evident that it is impossible to transform all the heat into work, because in that case it would be necessary in the original equation to make the fraction $\frac{T_2}{T_1} = 0$, that is to make T_2, which is the temperature of the refrigerator employed, equal to absolute zero, which is not possible in practice [1] for reasons which we have explained more than once (pp. 7 and 25).

OPTICAL PROPERTIES OF GASES

SPECTROSCOPY. If the rays of the sun are allowed to enter a dark chamber through a hole, they may be collected directly on a sheet of cardboard placed perpendicular to the rays, a large spot of light being thus obtained. If, however, the luminous rays are first passed through a prism, the spot on the card becomes elongated into a coloured streak, violet at one end and red at the other, while the colours of intermediate parts pass gradually through blue, green, yellow, and orange. The white light has been dispersed, and since the various waves composing white light are refracted unequally by the prism, the violet rays of smaller wave-length being most refracted and the red rays of greater wave-length least refracted, the colours corresponding with the various wave-lengths will be separated on the screen and will form together a continuous coloured spectrum.[2] If the white light before entering the prism is passed through a red glass, this absorbs all the other coloured rays and allows the red rays only to pass. If these are then refracted by a second prism, they produce simply a red spot on the cardboard in the precise position where the red coloration was found in the preceding complete spectrum. If green rays pass into the prism a green spot and no other colour is obtained in the position where the green coloration was in the complete spectrum of the white light, and so on.

This shows that the ethereal waves of various lengths corresponding with various colours are refracted through different angles, and that, in fact, the minimum refraction is shown by the red light and the maximum by the violet light. Bearing in mind this fundamental idea of the refraction of light, we may study how gases behave when rendered incandescent and luminous by strong heating, using for this purpose the spectroscope, illustrated on p. 58 (Fig. 18).

The light emitted by incandescent gases is different from that produced by liquid and solid substances or by the same gases when liquefied or solidified. The latter emit luminous rays of all wave-lengths and thus give a continuous spectrum. The light emitted by incandescent gases is formed of a few rays of definite wave-length, which, after passing through the prism of the

---

[1] If in the equation showing the efficiency of Carnot's cycle we take an infinitely small temperature, dT, and express the work in thermal units, using the product of the infinitely small pressure, dp, and the infinitely small increment of volume, dv, then we obtain the expression: $\frac{dp - dv}{Q} = \frac{dT}{T}$ and consequently $\frac{dT}{dp} = \frac{Tdv}{Q}$. This is Clapeyron's equation, which thus expresses quantitatively the *mobile equilibrium*, and may also be applied to changes of state (fusion, etc.), and generally to all cases where there is a supply or evolution of heat, differences of temperature, of pressure, and of work.

[2] At the two ends of the coloured *visible spectrum* non-visible zones may be detected: beyond the red rays are heat rays which raise the temperature of a thermometer placed there, while the ultra-violet rays exhibit great chemical activity, influencing a photographic plate and colouring a paraphenylenediamine nitrate paper.

spectroscope, give a dark spectrum with a few luminous coloured lines, characteristic for each gas or substance. They give, indeed, *emission spectra.* These lines appear in the spectroscope when a minimal trace of the substance to be studied is placed in a Bunsen flame. The incandescent and luminous gases which are immediately formed produce the emission spectrum.

We are thus able to discover and distinguish various substances even when mixed together, without the necessity for previous separation.

Spectroscopic studies were first rationally conducted by Foucault, Talbot, Wheatstone, etc., but systematic spectral analysis was initiated by Kirchhoff and Bunsen in 1859, by studying and identifying the spectra characteristic of various substances heated to high temperatures. In 1865 Plücker and Hittorf found for the first time that the same gas is able to give different spectra according to the temperature. At relatively low temperatures, the gases actually give continuous spectra; on raising the temperature, characteristic emission spectra are obtained for each gas; on raising the temperature still further, spectra are obtained with many coloured lines collected into groups, which are no longer characteristic. Helmholtz, Moser, Ciamician, and Wiedemann found that chemical compounds give spectra with coloured lines in groups which have nothing in common with the spectra of their elementary components.

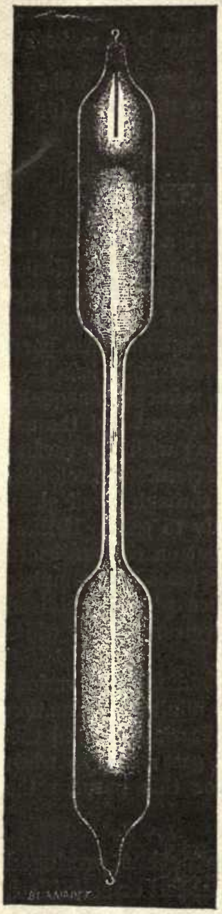


FIG. 16.

Nevertheless Bunsen and Kirchhoff observed that various chemical compounds of the same alkali or alkaline earth metals (*e. g.*, chloride, carbonate, and oxide of barium, etc.) all gave the same spectrum corresponding with that of the metal (barium); they were, however, unable to explain this behaviour, which was not in harmony with Helmholtz's observation that chemical compounds do not give emission spectra with isolated characteristic lines.

In 1864 Mitscherlich showed that this fact observed by Bunsen was due to the decomposition in the flame of the various compounds of the same metal. Thus the various salts of barium decompose or dissociate, and all give the spectrum of barium oxide or of barium itself.

An explanation or theory of spectroscopic phenomena was first given in 1865 by Lecocq de Boisbaudran[1]—but his hypothesis was erroneous—whilst in 1878 Maxwell published a more rational hypothesis in harmony with the kinetic theory of gases. The atoms which collide in the interior of the molecule produce vibrations of the cosmic ether, but the molecules also collide with one another at considerably longer intervals, influencing the oscillations produced by the atoms. In this latter case, therefore, in addition to the striations or lines of the spectrum due to the vibrations of the colliding atoms, we have also luminous groups of lines or continuous portions of the spectrum due to the collision of the molecules. Further, if the gas is rarefied in a suitable tube (Plücker-Geissler tube) such as is indicated in Fig. 16, so that the electric discharge is formed in a capillary tube where there are only a few molecules,

---

[1] He imagined that the atoms had projections, which on impact against the sides of the vessel or against a plane produced waves of determinate length, and thus in the case of an atom with several projections there would be waves of more than one wave-length, which would be characteristic and different for different gases. This hypothesis, however, could not be maintained because the wave-lengths producing such characteristic luminous lines are independent of variations of temperature, whilst according to the hypothesis they would depend upon the duration of the rotation and undulation of the atoms, which duration could not be independent of the temperature.

then the molecular impacts are much fewer and the spectrum of the atoms, formed of striations or isolated luminous lines, is better seen. In Fig. 17 is shown the arrangement of a Plücker tube on a suitable support for passing the electric discharge.

Kayser attempted to show that the number of lines of the emission spectrum of an element was a function of the atomic weight, but there are many gaps in his conclusions. Certain regularities were found only with the first groups of the *periodic system* of the elements, it being observed that, for each group, increase of the atomic weights of the elements is accompanied by displacement of the spectroscopic lines from the violet towards the red. From one group to another, on the other hand, the displacement takes place in a marked manner towards the shorter undulations, that is, towards the violet, and the lines approach one another and become more numerous, so that the maximum accumulation of lines is found in the ultra-violet portion of the spectrum. According to Reinganum (1904) the regularities are more evident if instead of the atomic weights we take into consideration the atomic volumes, that is, the volumes in c.c. occupied by such quantity in grams of a solid element as corresponds with the atomic weight.

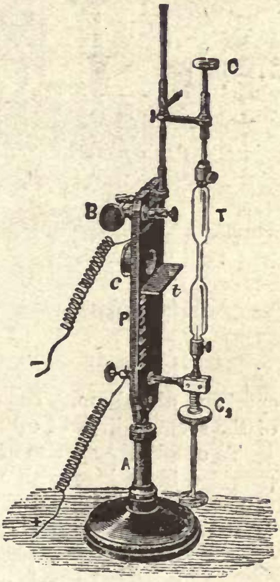


FIG. 17.

It has now been established that spectra are produced, not by the atoms, but by ions (*see later*, Ionic theory) derived from the atoms or molecules. Gaseous ions give electric spectra, whereas electrolytic ions or solid or dissolved substances give absorption or phosphorescence spectra. In general, every element yields a complex spectrum, which varies according to the method used to produce it. Flame spectra differ from spark spectra, and the latter, for one and the same element, change with the auto-induction and with the current intensity; arc spectra are unlike spark spectra.

The emission spectrum is composed solely of lines or groups of lines corresponding with given elements. There are, however, other spectra called *absorption spectra*, which are continuous spectra containing luminous lines (of the emission spectrum). White light gives a continuous spectrum, but if it is passed through an incandescent gas, only those waves of the spectrum will pass which are not isochronous with those of the gaseous incandescent element; those which are isochronous (in the white light of the incandescent gas) will interfere, and in the positions corresponding with such wave-lengths black lines will be observed in the spectrum.

There are also other absorption spectra which are characteristic of solutions of various coloured organic substances. (*Translator's Note.*—And also of certain inorganic solutions.)

In order to study these questions in the laboratory, use is made of the spectroscope (Fig. 18) invented by Bunsen and Kirchhoff. On a table carried by a pedestal is placed a prism of flint glass with angles of 60°. On to one face of the prism there converges the observation tube *B*, which collects the spectrum formed from the luminous rays entering through the collimator *A* and also the light from the millimetre scale reflected from the same face of the prism and proceeding from the tube *C*. The substance under examination is rendered incandescent by a non-luminous flame F, and the light emitted enters the tube A through a vertical adjustable slit. The rays are rendered parallel by a collimating lens placed in the tube A near to the prism and at such a distance from the slit that the latter is exactly at the focus of the lens. The rays, which are now parallel, meet one face of the prism at the angle of minimum refraction, the spectrum being thus rendered sharper. The spectrum is observed through the observation tube B, which is so adjusted horizontally that the rays of the spectrum are in the centre of the field of vision. In order to determine the position of the spectral lines, a tube C is used which carries at its extremity S, a horizontal slit through which the rays of a luminous flame enter and immediately impinge on a millimetre scale photographed on a glass plate. The divisions of this scale are reflected from the face of the prism and can be observed through the telescope B, together with the spectrum. In order to compare the position of the spectral lines of different substances, the scale in the tube C is adjusted in such a manner that the division marked 50 corresponds with the yellow line of the emission spectrum of sodium. The scale remains definitely fixed at this point, and the positions of the spectral lines of other substances can thus be determined.

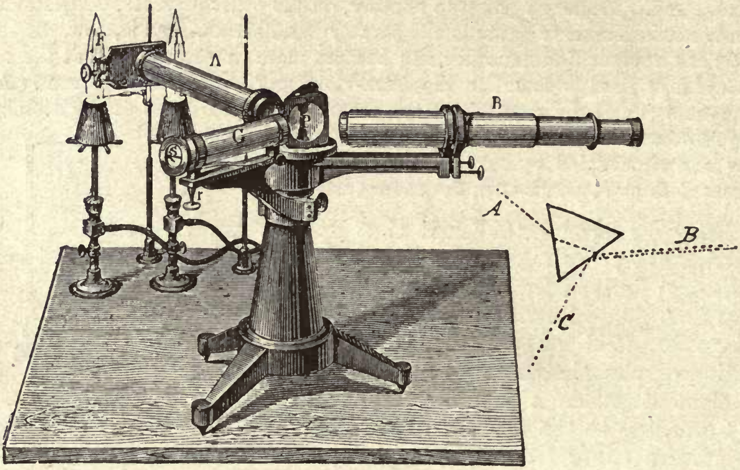


FIG. 18.

To obtain the spectra of liquid or dissolved substances, these are placed in a test-tube provided in its base with a platinum point (Fig. 19) united to one pole of a Ruhmkorff coil. Another platinum wire is carried close to the surface of the liquid and united with the other pole of the coil, so that sparks pass which give the spectrum corresponding with the liquid or dissolved substances in the spray which is formed.

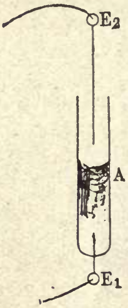


FIG. 19.

The following elements were first discovered by means of their flame spectra: rubidium and cæsium by Kirchhoff and Bunsen, thallium by Crookes, and indium by Reich and Richter. With the more sensitive spark spectrum Lecoq de Boisbaudran discovered gallium, while with cathodic phosphorescence spectra Crookes discovered the rare earths and also europium, although the latter gave abnormal lines in the phosphorescence spectrum. Didymium was detected by Gladstone with the help of absorption spectra of its solutions, and by the same method Auer discovered prascodymium and Lecoq de Boisbaudran (who first used absorption spectra) samarium; later dysprosium, holmium, neo-erbium, and thulium were found. Luthenium was discovered with the help of the voltaic arc spectrum. Urbain discovered celsium (1911) by means of the magnetic balance, which was used by Curie and Chénevaux to distinguish between substances of different atomic weights, and is far more sensitive than the ordinary balance. Paramagnetism or diamagnetism is a fundamental property characteristic of the molecules of substances in the same way as groups of coloured compounds are characterised by absorption spectra; thus, the hexamminocobalt salts or the ferrocyanides form a group in which the molecular magnetism is constant.

If the white light of a luminous body, such as the sun, electric arc, etc., is passed through a gas heated to a high temperature (incandescent gas), we obtain characteristic absorption lines in the continuous spectrum of the white light, black lines which correspond in the scale of the spectroscope exactly in position with those of the emission spectra of the same incandescent gas. The experiment is carried out practically by placing the substance to be studied on one of the carbons of an arc lamp.

In this manner is explained the fact that the white light of the incandescent solar nucleus, after passing through the solar atmosphere formed of many strongly heated gases, gives a continuous spectrum divided by numerous black lines. These were first observed by Wollaston and correspond with the gaseous elements occurring in the solar photosphere. They were then studied by Fraunhofer, who assigned letters of the alphabet to the principal lines, the sodium line being denoted by D. Bunsen and Kirchhoff then studied many more of them. The following elements, which we will denote by their symbols only (*see* Table, p. 43), were thus found with certainty in the sun: Na, Fe, Ca, Cr, Ni, Ba, Zn, Co, H, Mn, Ti, Al, Sr, Pb, Cd, Ce, U, W, Pd, Mo; the following are also probably present: In, Li, Rb, Bi, Sn, Ag, Be, La, Y. The presence of carbon, oxygen, and nitrogen is, on the other hand, disputed, but most probably at such elevated temperatures (supposed by Moissan in 1906 to be 4000–6500°) the characteristic lines of these elements due to the impacts of the simple atoms are no longer obtained, and it may be supposed that under such conditions these atoms are finally split into still smaller particles. The above-mentioned yellow sodium line is, in fact, formed of two lines very close together, and similarly other atoms give multiple lines, which perhaps denote the impacts of still smaller particles. By means of spectral analysis we are able to identify minimal quantities of substances. Thus the spectrum will reveal $\frac{1}{3,000,000,000}$ of a gram of sodium.

CHEMICAL EQUATIONS

The chemical reactions which occur between various substances, simple or compound, may be represented by means of equations, which are just as rigorous as algebraic equations. The reactions always occur between chemical particles, and therefore between definite weights of the reacting substances. Since no matter is lost in any reaction, the chemical equation must also represent quantitatively the equality between the weights of the reacting substances and those of the new substances which are formed.

Thus, for example, the reaction which occurs between one molecule of chlorine and one molecule of hydrogen, giving hydrochloric acid, may be represented by the following equation: $H_2 + Cl_2 = HCl + HCl = 2\,(HCl)$.

All the atoms of the first member of this equation are found again, differently grouped, in the second member, and the total weight of the molecules of the first is equal to the total weight of the molecules of the second. Thus these equations express to us, in a simple and exact manner, one of the most important laws of chemistry and of nature in general, which says that in all transformations of matter nothing is created and nothing is lost. Thus:

$$\begin{array}{rl} & H_2 + Cl_2 = 2HCl \\ \text{weight} & \underbrace{2 + 71}_{73} = \underbrace{2 \times 36{\cdot}5}_{73} \end{array} \qquad \begin{array}{rl} & H_2SO_4 + Zn = ZnSO_4 + H_2 \\ \text{weight} & \underbrace{98 + 65}_{163} = \underbrace{161 \text{ (zinc sulphate)} + 2}_{163} \end{array}$$

From this equation we see clearly that in order to prepare 161 grms. of zinc sulphate and 2 grms. of hydrogen, 98 grms. of sulphuric acid and 65 grms. of zinc are required.

In other cases chemical equations serve to solve important practical problems. For example, to determine in advance whether sodium chloride or potassium chloride is more suitable for the manufacture of hydrochloric acid (supposing that the prices of these two salts are equal), we find for the chemical reaction between the salt and sulphuric acid the following equation :

$$\begin{array}{ccccccc} NaCl & + & H_2SO_4 & = & NaHSO_4 & + & HCl \\ 58{\cdot}5 & + & 98 & = & 120 & + & 36{\cdot}5 \end{array} \quad \text{or} \quad \begin{array}{ccccccc} KCl & + & H_2SO_4 & = & KHSO_4 & + & HCl \\ 74{\cdot}5 & + & 98 & = & 136 & + & 36{\cdot}5 \end{array}$$

Now we see that with the same quantity (98) of sulphuric acid, in one case 58·5 parts by weight of sodium chloride and in the other case 74·5 parts by weight of potassium chloride are needed in order to obtain the same quantity, 36·5 parts, of hydrochloric acid. It will thus be better to employ sodium chloride even if this costs as much as potassium chloride; the practical advantage is, however, still greater, because sodium chloride costs much the less.

FUNDAMENTAL PRINCIPLES OF THERMOCHEMISTRY

When we write a chemical equation, we do not express completely the chemical phenomenon. Though the equation evidently expresses a transformation of matter, we have still no idea of the changes which occur in the inherent energy of the substances themselves, and which are closely connected with all chemical phenomena.

The chemical energy or internal energy of the substances, being indestructible, will be found in equal quantities, though partly under different forms, before and after a given chemical reaction has occurred.[1]

Modifications in the chemical state of one or more substances are always accompanied by development or absorption of energy, which is generally measurable in the form of heat. Hence the name thermochemistry given to the study of chemical reactions with the measurement of the thermal changes.

Lavoisier and Laplace argued, without experimental demonstration, that in order to decompose a substance into its components, there would be required the same quantity of heat as was developed in its formation. The experimental demonstration of this important conception was not undertaken until the work of G. H. Hess in about the year 1840, and thus at an epoch anterior to the discovery of the law of the conservation of energy by R. Mayer in 1842.

By studying the formation of ammonium sulphate, Hess demonstrated experimentally that the total heat developed in a chemical process is always the same however the reaction occurs—whether in one step or in several phases. Hess may be considered to be the founder of thermochemistry.[2]

The work of Andrews (1841–1848), of Graham (1843–1845), and of Grassi (1845) did not advance the progress of thermochemistry very much. In France, however, Favre and Silbermann undertook extensive and important thermochemical researches which extended over some years (1844–1850), and proved that there are also chemical reactions

---

[1] Chemical energy is of the greatest importance throughout the large economy of nature. Firstly, because it is durable: thus, a piece of coal provided by a plant which accumulated radiant energy from the sun is conserved for thousands of years in the depths of the earth without losing any of its energy, which may be utilised in combustion. Secondly, because chemical energy is ordinarily found in very concentrated forms; in fact, if one were able, for example, to transform completely into mechanical work the heat of combustion of a single gram of hydrogen, one would be able to raise a weight of 14,000 kilos to a height of one metre. It is thus evident that chemical energy occurs in a form which is very convenient for transportation, because it is greatly concentrated. Boyle, Lavoisier, and Laplace carried out chemical experiments in which the heat developed by animal organisms was measured, and similar experiments were also made in 1779 by Crawford, in 1822 by Dulong, and in 1824 by Despretz. Furthermore, Davy in 1813 and Rumford in 1817 determined directly the calorific powers of solid, liquid, and gaseous fuels.

[2] By a strange fatality and historic coincidence, Hess, who in 1840 had rediscovered the valuable work of Richter which leads to the first fundamental laws of chemistry (equivalents, etc.) and which was unjustly attributed by Berzelius to Wenzel, was in his turn forgotten by his contemporaries, whilst the great importance of his work was only recalled and pointed out by Ostwald in 1886.

in the course of which heat is absorbed, whilst until that time it had been believed that chemical combination was always accompanied by evolution of heat. Reactions which occur with evolution of heat were then called *exothermic* reactions, whilst those which occur with absorption of heat were termed *endothermic*.

In 1853–1854 J. Thomsen established the foundations of a thermochemical system by applying for the first time the principles of the mechanical theory of heat. He showed that the thermochemical equivalent of a substance (or internal energy, supposing this all to be transformed into heat) has always the same value under the same conditions.

If heat is developed during a chemical combination with or without increase of volume (external work), the internal energy must diminish by the corresponding amount. The thermal tonality, that is, the evolution or absorption of heat, and the heat corresponding with the external work (increase of volume) of a chemical process must then be equal to the internal energy of the reacting substances, less the internal energy remaining in the products of the reaction. The thermal tonality is proportional to the quantities of the reacting substances.

In 1851–1852 Woods carried out similar work independently of that of Thomsen, and arrived at the same results.

When solid and liquid substances react with production of a gas, the external work is increased by 24·19 calories for every litre of increase of volume (*see* p. 27).

The true founder of thermochemistry in France was Berthelot. From 1865 up to the last few years, together with his numerous pupils, who are disseminated throughout Europe, he has enriched this branch of chemistry by numerous and important experiments which have led to a complete system from which the fundamental laws of thermochemistry have been deduced. These laws were collected by Berthelot, together with his more important work, in two volumes published in 1876. He enunciated the three following general laws: (1) *The heat developed in a chemical process is the measure of the chemical and physical work produced*[1]; (2) *the thermal effect*

---

[1] The calorific unit which serves as the basis of all thermochemical measurements is either the *small calorie* (cal.), which represents the heat required to raise the temperature of 1 grm. of water from 0° to 1°, or the *large Calorie* (Cal.) of Berthelot, which expresses the heat required to raise the temperature of 1 kilo of water from 0° to 1° and is equal to 1000 cals. Finally, Ostwald has advised the acceptance of the rational calorie proposed by Schuller and Wartha in 1877, which expresses the quantity of heat necessary to raise 1 grm. of water from 0° to 100°, and is denoted by the letter K to distinguish it from the others; this is equal to 100 small calories.

It was more especially the work of Joule which led to the exact determination of the mechanical equivalent of heat. It was then generally confirmed that 1 Calorie could accomplish the work of 427 kilogram-metres (1 kilogram-metre is the work necessary to raise 1 kilo to a height of 1 metre); and, *vice versa*, the mechanical work of 427 kilogram-metres corresponds with exactly 1 Cal. of heat.

More rationally, the *joule* (j) is used to-day and refers to the fundamental unit of work, the *erg*, or, better still, use is made of the *kilojoule*, which is equal to 1000 j and corresponds with 239 cals.

We have already seen (p. 38), in considering the kinetic theory of gases, that the kinetic energy (E) of a body $= \frac{1}{2}\, m \,.\, c^2$, and since all forms of energy are equivalent, they may all be represented by or referred to this formula. If we wish to deduce from this formula the rational unit of energy, we must substitute for the value m 1 grm., that is, the one-thousandth part of the unit of weight preserved at Paris and consisting of a block of platinum, the weight of which is fixed at 1 kilo; the velocity (c) is deduced from a simple formula $c = \frac{L}{T}$, where L is the length of the path, measured in centimetres, and T the time, measured in seconds. Then for 1 grm. moving with a velocity of 1 cm. per second, we have $E = \frac{1}{2} \,.1\,.\, 1^2 = \frac{1}{2}$. Transforming into units the value of the energy resulting from this formula $\left(\frac{1}{2} \times 2 = 1\right)$, we shall find that the unit of energy is double the amount of energy contained in 1 grm. of any substance, moving with the velocity of 1 cm. per second. The unit of force is called the *dyne* (*see* p. 27), and the work which corresponds with one dyne is called the *erg* (unit of work), which has a very small value. In order to form an idea of the erg, it will suffice to imagine a mass of 100 grms. projected with a velocity of 1000 cm. per second, which corresponds with 50,000,000 ergs. For practical convenience, calculations are made with units of 10,000,000 ($= 10^7$) ergs, and this quantity or practical unit is called the *joule* and denoted by j.

The work of Mayer and of Joule determined the ratio between work and heat, and this *of a chemical process depends only upon the difference between the thermal state before and after the reaction, whatever the intermediate reactions which have occurred* (law of Hess); (3) *every chemical transformation which occurs without the intervention of energy from outside, tends towards the formation of those compounds or systems of compounds in which the largest quantity of heat is evolved* (principle of greatest work). This last principle, which was enunciated by Thomsen in 1853, was then developed by Berthelot, but in the last few years it has proved to be in contradiction to many reactions (reversible actions, actions of catalysts, chemical equilibria, etc., *see below*), and van't Hoff, Nernst, and others have shown that it is insufficient or have accepted it as exact only on starting from absolute zero for solid reactions (that is, when the product of the reaction separates as an insoluble solid) and when the thermal tonality is independent of the temperature (*see below*, chapter on Affinity).

From 1869 to 1882 Thomsen carried out further very numerous experiments, the results of which are collected into four volumes published in 1882–1884, and all confirm these fundamental laws.

Stohmann, in Germany, after a large number of experiments on thermochemistry applied to physiological chemistry, obtained results in perfect harmony with the above-mentioned laws.

Important improvements in the apparatus used in the more exact thermochemical research are due to Thomsen and more especially to Berthelot. Berthelot's calorimeter or bomb is used in all laboratories and has also been of use in the study of numerous organic compounds. We give a description of it in the chapter on carbon and fuels. The chemical reactions are carried out in a closed metallic receiver immersed in a measured quantity of water, the temperature of which is noted both before and after the reaction.

There is a general agreement to-day to refer the thermal tonality of a substance or of a chemical reaction to gram-molecules of the substances in question (in mols., *see* p. 26), or in the case of metals to gram-atoms; they may also be referred to gram-equivalents.

We will now follow some reactions thermochemically. The equation:

$$Pb + I_2 = PbI_2 + 39{,}800 \text{ cals.},$$

signifies that the internal energy of 207 grms. of Pb (atomic weight 207) + the internal energy of 2 × 127 grms. of iodine (atomic weight 127) = the internal energy of 460·6 grms. of PbI_2 (molecular weight) + 39,800 calories developed in the reaction. Thus $PbI_2 = -39{,}800$ cals., that is, PbI_2 contains 39,800 calories less than the free components and, in order to regain Pb and I_2 from it, it would be necessary to employ 39,800 cals. which were evolved during its formation.

In the formation of 18 grms. (mol. wt.) of water at 0° starting from 2 grms. of hydrogen and 16 grms. of oxygen, 68,400 cals. are developed, and thus H_2O (liquid) = − 68,400 cals. (or 286 Kj., since 1 Kj. = 239 cals.). If, on the other hand, 18 grms. of water vapour at 100° are considered, it is necessary to deduct 100 calories, which are developed for each

---

ratio was corrected later by very exact determinations, so that we know to-day that one small calorie (referred to 1 grm. of water at 18°) corresponds with 41,890,000 ergs, that is, 1 calorie = 4·18 j, while the rational (centesimal) calorie K = 418 j. This is the most exact expression for the mechanical equivalent of heat measured with the fundamental unit of work, that is, the erg, or with the joule, j. Since the kilojoule (Kj) = 1000 j, 1 cal. = 0·00418 Kj. = $\frac{1}{239}$ Kj., so that 1 Kj. = 239 cals. On the other hand, 1 cal. corresponds with 427 kilogram-metres of work.

One horse-power (h.p.) corresponds with 75 kilogram-metres per second (= 270,000 per hour), and thus 1 Cal. corresponds with 5·69 horse-power seconds (= 427 : 75), and 1 horse-power hour with 630 Cal. With a good steam-engine 1 horse-power hour is obtained with about 3–4 kilos of coal, according to the size of the engine, and will thus cost from 1·2*d.* to 1·5*d.* in Italy. With gas engines 1 horse-power hour costs less than 0·3*d.* to 0·4*d.* The price of 1 electrical horse-power hour (with transport of energy) varies very much (from ½*d.* to 1·2*d.*). It may be remembered that a horse-power corresponds with 734 watts or 0·734 kilowatt.

gram of water when cooled from 100° to 0°, and also the heat of evaporation, which is 537 cals. for each gram of water; the expression now becomes:

$$H_2O \text{ (vapour)} = -57{,}000 \text{ cals. } [i.e., 68{,}400 - (637 \times 18)] \text{ also referred to 18 grms.}$$

This result, and also that obtained in the case of liquid water, must be corrected still further to allow for the fact that, starting from gaseous substances, and in fact from 1 mol. (22·412 litres = 2 grms.) of hydrogen and ½ mol. of oxygen (11·206 litres), we obtain liquid water. There has thus been a diminution in volume of 1½ mols., that is, 33·618 litres, and the corresponding quantity of heat has consequently been developed; this heat can be calculated, as we know that 1 litre-atmosphere corresponds with 24·19 cals. (*see* p. 27). Thus the true thermal tonality of the formation of H_2O (liquid) will be:

$$68{,}400 - (24{\cdot}19 \times 33{\cdot}618) = 68{,}400 - 814 = 67{,}586 \text{ cals.}$$

The true thermal tonality for H_2O vapour will be 57,000 cals. diminished by the heat corresponding with ½ mol. by volume, because 1 mol. of water vapour results from 1½ mols. of hydrogen and oxygen.

When a gas reacts on a liquid it is sometimes necessary to take into account the heat of solution of the gas in the liquid.

Thus, if we allow aqueous solutions of potassium hydroxide and HCl to react we shall have the following equation, the thermal tonality of which in this case expresses the heat of neutralisation:

$$\text{KOH aq.} + \text{HCl aq.} = \text{KCl aq.} + H_2O + 57{\cdot}35 \text{ Kj. } (= 13{,}700 \text{ cals.}).$$

If an aqueous solution of KOH reacts directly with gaseous HCl the equation will be:

$$\text{KOH aq.} + \text{HCl gas} = \text{KCl aq.} + H_2O + 129{\cdot}91 \text{ Kj. } (= 31{,}060 \text{ cals.}).$$

According to this second equation we have a development of 72·38 Kj. (= 17,360 cals.) more heat, and this expresses the heat of solution of gaseous HCl in water. In the thermal effect which results from these reactions the work of dissociation of the reacting molecules into the corresponding simple atoms—a process which requires considerable quantities of heat—is also included.

Thus, the heat which is actually measured represents the difference between the heats of combination of the reacting atoms and the heats of dissociation of the reacting molecules.

The second law of thermochemistry (of Hess) is also called the law of the constant sum of the heat effects, and says that the final thermal effect of a complete reaction is the same, whether the reaction occurs in one phase or in a number of phases, that is, the energy difference between two states of a chemical system is independent of the cycle through which it has passed from the one state to the other. If, for example, to an aqueous solution of 1 grm.-molecule of phosphoric acid, H_3PO_4 (tribasic acid), an aqueous solution of 3 grm.-molecules of sodium hydroxide, 3NaOH, is added, trisodium phosphate is formed with development of 142·4 Kj. (= 34,030 cals.):

$$3\text{NaOH aq.} + H_3PO_4 \text{ aq.} = Na_3PO_4 \text{ aq.} + 3H_2O + 142{\cdot}4 \text{ Kj.}$$

If, on the other hand, we add the three molecules of NaOH one at a time, we have the following three phases of the reaction, which, however, lead to the same final thermal result:

$$\begin{aligned}
\text{NaOH aq.} + H_3PO_4 \text{ aq.} &= NaH_2PO_4 \text{ aq.} + H_2O + 14{,}829 \text{ cals.}\\
\text{NaOH aq.} + NaH_2PO_4 \text{ aq.} &= Na_2HPO_4 \text{ aq.} + H_2O + 12{,}251 \text{ cals.}\\
\text{NaOH aq.} + Na_2HPO_4 \text{ aq.} &= Na_3PO_4 \text{ aq.} + H_2O + 6{,}950 \text{ cals.}
\end{aligned}$$

The sum of the amounts of heat liberated by the three intermediate reactions is 34,030 cals. and corresponds with the heat produced when the reaction takes place in a single phase.

The heat of formation of the intermediate compounds of a given reaction can be deduced by an *indirect method* from the original and final thermochemical systems of the reaction. For example: though the heat of formation of carbon monoxide, $C + O = CO$, cannot be determined directly, yet it can be deduced indirectly from the knowledge that $C + O_2 = CO_2 + 97,000$ cals. (405·8 Kj.) and that $CO + O = CO_2 + 67,850$ cals. (284·5 Kj.); by subtracting the one phase from the other we have the other phase :

$$C + O = CO + 29,150 \text{ cals. } (i.e., 97,000 - 67,850).$$

This indirect method gives exact results and is often employed for complicated chemical systems, especially for the indirect determination of the thermal effect of reactions which cannot be obtained directly, or in special cases in which the practical measurement of the thermal effect of such reactions is not possible.

Berthelot maintained that the heat developed during the combination of two substances is proportional to their affinity, but this is not always correct, as was shown by Le Chatelier, who elucidated the bearing of the principle of the resistance to reaction, which he had deduced thermodynamically, on chemical reactions. This principle is closely connected with the principle of mobile equilibrium enunciated by van't Hoff for the various physical states of matter.

This rule states that every change of one of the factors which regulate a chemical-physical system in equilibrium produces transformations in the system which are opposed to the action of the modifying factor. Thus, for example, by altering the temperature of a liquid, for instance, by heating it, evaporation occurs, that is to say, a phenomenon which absorbs heat. Two substances which combine with evolution of heat tend to dissociate when reheated, that is, to be transformed into their components with absorption of heat, and since the majority of known substances are formed with evolution of heat, they are decomposed at temperatures more or less elevated, whereas substances which absorb heat during combination (endothermic substances) are not dissociated by rise of temperature (in fact they are generally formed at high temperatures), but on the contrary become more stable. We thus see that the belief of many, that at very high temperatures, for instance, in the sun, all substances have a tendency to dissociate into their respective elements, is erroneous, this being true only for substances formed with development of heat, and not for those which absorb heat during formation.

Rhombic sulphur is transformed into the monoclinic variety with absorption of heat, so that when heated, rhombic sulphur is transformed into the monoclinic form (*see also* chapter on Sulphur).

By Le Chatelier's principle and with the aid of thermodynamics, one can always foresee in which sense a chemical reaction will proceed, or whether such a reaction is possible or not. One cannot, however, always bring about a reaction which is theoretically possible, because of the so-called passive resistances (friction, capillarity, ionisation, etc.), which often cannot be calculated thermodynamically. Thus alcohol does not burn in oxygen at the temperature of liquid air (— 190°), and under the same conditions sodium does not react with alcohol or chlorine with hydrogen, etc., and it is well that it is so, because if all reactions theoretically possible were to occur in nature, all combustible or oxidisable substances would burn, even at ordinary temperatures, and our planet would become a veritable inferno, uninhabitable for vegetables and animals.

Temperature has a great influence on chemical reactions, and in general the velocity of reaction is greatly diminished when the temperature is lowered. While the temperature rises according to an arithmetical series the velocity increases geometrically. On raising the temperature by 10°, the velocity of reaction increases to double or treble its former value (*see below*).

CHEMICAL EQUILIBRIA AND VELOCITIES OF REACTION

In chemical reactions we have many evident examples, and also others which are less evident, in which the reacting substances do not combine completely, but only partially (*partial reactions* which are in contradiction to the third principle of thermodynamics, enunciated by Berthelot). In such cases it is supposed that under given conditions a part of the product of reaction is again dissociated into its components, thus establishing a chemical equilibrium between the reaction proceeding in one sense and that proceeding in the opposite sense; hence in all such phenomena one can no longer speak of a static equilibrium, but rather of an equilibrium kinetic in character.

The Swedes, Guldberg and Waage, inspired by the conceptions of Berthollet, published in 1867 an important work ("Études sur les affinités chimiques"), in which they placed the equilibrium of chemical reactions on a mathematical basis. This work passed unobserved, and in 1873 an Englishman, Jellet, came to analogous conclusions. It was only in 1877 that van't Hoff pointed out the great chemical importance of these studies.

In the study of chemical equilibrium it is necessary to fix clearly the conception of the concentration of substances coming into play during reactions. It is not the absolute quantities of the mass of reacting substances which are of interest, but rather their relative mass per unit of volume. The rational method of expressing concentration is by the number of gram-molecules (*see* p. 26) contained in a unit of volume (ordinarily one litre).

One mol. of any gas at 0° and 760 mm. pressure occupies a volume of 22·412 litres (*see* p. 26), and its concentration, C, is given by

$$C = \frac{1}{22{\cdot}412} = 0{\cdot}044619.$$

Since, by the laws of Boyle and Gay-Lussac (*see* p. 26), the volume, v, of a gas at temperature T and pressure p is given by $v = \frac{V_0 p_0 T}{p \,.\, 273}$, at pressure p and absolute temperature T, these 22·412 litres will be:

$$v = \frac{22{\cdot}412\, p_0 T}{p \,.\, 273}$$

and consequently the concentration $C = \frac{273 \,.\, p}{22{\cdot}412\, p_0 T}$. When gaseous mixtures are considered in which one of the components has the percentage volume V and partial pressure p, whilst the total pressure is P, we have $p = \frac{V \,.\, P}{100}$, and thus the concentration of that component will be:

$$C = \frac{273\, PV}{100 \times 22{\cdot}412\, T} = \frac{0{\cdot}12181\, PV}{T}.$$

If the gas formula, $p\,v = R\,T$ (*see* p. 26), refers to one mol. of a substance, that is, to 22·412 litres, then, in all those cases in which n mols. of a substance are contained in that volume, we have $pv = n \,.\, RT$, and the concentration becomes:

$$C = \frac{n}{v} = \frac{p}{RT},$$

that is to say, the *concentration of a given quantity of substance is directly proportional to the pressure to which it is exposed, and inversely proportional to the absolute temperature and also to the volume*, that is:

$$\frac{C}{C_1} = \frac{p}{p_1} = \frac{T'}{T} = \frac{v_1}{v}.$$

In a mixture of gases in which the total pressure is P and the partial pressure of one of the components p, we have $pv = nRT$, and $Pv = NRT$, where n and N indicate the number of mols.; and since both for the mixture and for each of the component gases the volume and the temperature are common and equal, we deduce the equation: $\frac{p}{P} = \frac{n}{N}$, i. e., *the partial pressure, p, of one component is in the same ratio to the total pressure, P, of* *the mixture, as that of the number of mols., n, contained in volume v (and corresponding with p) to the total number of mols., N, or*

$$\frac{p}{P} = \frac{\frac{n}{v}}{\frac{N}{v}} = \frac{C}{\Sigma C};$$

this expression indicates that the *partial pressure of one component of a gaseous mixture is in the same ratio to the total pressure as its concentration is to the sum of the concentrations of the components.*

We may also write $C = \frac{p}{P}\Sigma C$, i. e., *the concentration of one of the components of a gaseous mixture is equal to the sum of the concentrations of all the components multiplied by the ratio between the partial and total pressures.*

We shall have occasion later to refer to these considerations of concentration not only for the following general considerations of chemical equilibria, but also when we study systematically certain important chemical reactions (*see* Sulphur Trioxide, etc.).

REVERSIBLE REACTIONS. Wenzel in 1777, and Berthollet in 1799 agreed that in some cases certain reactions are not completed, but a rigorous study of such chemical equilibria was only undertaken much later by Berthelot and Péan de Saint-Gilles in the case of the formation of esters, where it is easy to observe that a reaction may proceed in opposite directions. In such reversible reactions we replace the sign of equality in the equation by $\rightleftarrows$ or more simply by $\longleftrightarrow$, in order to indicate that the reaction may take place in the two senses. At certain temperatures hydrogen and iodine combine *in part* to form hydrogen iodide (HI), but the latter dissociates in part at the same temperature into H and I. This reversible reaction may be represented by the equation $H_2 + I_2 \rightleftarrows 2HI$.

In the study of chemical equilibria, it is necessary to distinguish cases in which the system is a one-phase system and forms a homogeneous equilibrium, from those in which there are several phases (*see below*, Theory of Phases), that is, when there are various states of aggregation or non-miscible liquids constituting a *heterogeneous equilibrium.*

To the establishment of a chemical equilibrium various factors contribute, these being the three *external factors*, temperature, pressure, and electro-motive force, and the three *internal factors*, physical state, chemical nature, and concentration of the substances. When even a single one of these factors is changed the state of equilibrium of the system becomes modified, whereas if two or more *equivalent factors* are altered at the same time, the equilibrium of the system may even remain unchanged. Catalytic action is not considered as one of the factors of equilibrium, because a reaction can occur even without the presence of a catalyst (*see below*), and even if this is present, the equilibrium is not displaced except in the case of a consequent modification of temperature.

The factors of equilibrium need not always be studied quantitatively in order to fix the conditions of equilibrium. A qualitative test which indicates in which sense the change of equilibrium is taking place, is often sufficient, as may be deduced by means of the principle of *mobile equilibrium* (*see* pp. 54 and 61) studied by van't Hoff for temperatures, and generalised by Le Chatelier for all the other factors of equilibrium.

We may add a few other examples to those already recorded in order to illustrate better this important *rule of the antitheses.* On raising, for example, the temperature, the equilibrium is displaced in a sense favourable to the reaction which absorbs heat. Substances which dissolve with absorption of heat are the more soluble the more they are heated. On the other hand, those which dissolve with evolution of heat are less soluble when hot than in the cold (anhydrous sodium sulphate, calcium hydroxide, etc.; *see* Part II., Freezing Mixtures). If the heat of solution of a salt is zero or very small, then the solubility is constant even when the temperature varies; this is the case with sodium chloride. Substances which are formed with evolution of heat are less stable when hot than in the cold, and above a certain temperature tend to dissociate into their components; this is the case with water, carbon dioxide ($CO_2 = CO + O$), calcium carbonate ($CaCO_3 = CaO + CO_2$), etc. Substances, on the other hand, which are formed with absorption of heat are more stable when hot than at low temperatures (for example, calcium carbide, acetylene, nitrogen peroxide, etc., *see* p. 64).

Increase of pressure displaces chemical equilibrium in that sense which conduces to a system requiring less pressure. Ice melts more easily under pressure, because on passing from the solid to the liquid state it diminishes in volume. Dissociations which lead to an increase of volume ($CaCO_3$ solid $=$ CaO solid $+$ CO_2 gas) are retarded or prevented by increase of pressure and facilitated by diminution of pressure. The reaction 2CO (gas) $=$ CO_2 (gas) $+$ C (solid), which leads to a diminution of volume, is facilitated by increase of pressure and rendered more difficult by reduction of pressure. Reactions which occur without change of volume are not influenced by the pressure (2HI gas, when heated $=$ H_2 gas $+$ I_2 gas).

Increase of *concentration* of one of the components of a system displaces the equilibrium in the direction of that system which diminishes the concentration of the component increased in concentration. Thus, in the system $H_2 + I_2 \rightleftarrows 2HI$, on increasing the concentration of H_2 or of I_2, there will be a greater formation of HI; this phenomenon is also called *mass action*. The reaction is still further facilitated if the concentration of the reaction products is diminished, *e. g.*, by eliminating the HI as fast as it is formed. This also explains why, in a liquid system, on causing a solution of sulphuric acid to react with one of barium chloride, complete transformation into barium sulphate occurs, because the latter is insoluble and separates. In the chapter on catalytic sulphur trioxide, we shall see the industrial importance of the study of such chemical equilibria, and we shall also see how, in the system

$$2SO_2 + O_2 \longleftrightarrow 2SO_3,$$

it has not been possible to apply the laws of equilibrium to their full extent.

Secondary reactions have a varied and often complex influence on the chemical equilibrium of a system, several systems in equilibrium being then present simultaneously. We shall have occasion later (Theory of Ions) to consider such cases.

A knowledge of *velocity of reaction* is also of great importance in the study of chemical equilibrium, and we may illustrate it by an example which was very exactly studied by Lemoine in 1877, viz., the action of hydrogen on iodine, with formation of hydrogen iodide (HI). At 270° the partial reaction occurs only after some months and at 300° after fifteen days. When, however, equimolecular quantities of hydrogen and iodine ($H_2 + I_2$) are heated together at 440°, the maximum quantity of hydrogen iodide, amounting to 79 per cent. of the reacting substances, is formed in three or four hours; the residual 21 per cent. remains apparently unaltered (kinetic equilibrium). At high temperatures the HI diminishes steadily in amount, and with every temperature there corresponds a certain relation between HI, H, and I. It is evident that rise of temperature is accompanied by a dissociation of HI into its components, and we may suppose that this dissociation takes place even at temperatures lower than 440°, but that up to that temperature the quantity of HI formed is greater than the amount dissociated, whilst above 440° the quantity of HI dissociating is more than that which is formed.

The degree of reaction and of dissociation is constant for a given temperature. Thus, on heating pure hydrogen iodide in a closed tube at a temperature of

440°, after some hours 21 per cent. of it is found to be dissociated into H and I. The state of equilibrium for a given temperature and pressure between the two systems, that is, $H_2 + I_2 = 2HI$ and $2HI = H_2 + I_2$, or $H_2 + I_2 \rightleftarrows 2HI$, is reached, when in unit of time the amounts of each system transformed into the other are equal.

For each temperature the quantity of the product of the reaction is a function of the time. Thus we may call velocity of reaction (v), the change of concentration (C) of one of the components of the system per unit of time, and we may represent it thus: $v = \frac{dC}{dT}$.

The velocity of reaction depends on the nature of the substances and on their concentration (or active mass), because the greater the latter the more frequently do the molecules collide and combine. The number of impacts between the molecules is proportional not merely to the concentration, but also to the velocity of the molecules and therefore to the temperature.

If we suppose the temperature to be constant in the reaction between one molecule of H_2 and one molecule of I_2 (= 2HI), and denote the concentrations of these in a given volume by C_{H_2} and C_{I_2}, then the velocity of reaction, v, will be proportional to the concentration and to a certain constant factor, k, or coefficient of velocity, which varies for each reaction; we have thus: $v = k \, . \, C_{H_2} \, . \, C_{I_2}$. For the more complex reaction

$$H_2O + NO_2 + NO + O_2 = 2NO_3H, \text{ we have } v = k \, . \, C_{H_2O} \, . \, C_{NO_2} \, . \, C_{NO} \, . \, C_{O_2},$$

that is to say, the velocity of reaction is equal to the product of the concentrations multiplied by the velocity coefficient. If one of the components of a reaction takes part by means of several molecules, as, for example, in $2H_2 + O_2 = 2H_2O$, we should have $v = k \, . \, C_{H_2} \, . \, C_{H_2} \, . \, C_{O_2}$ or $v = k \, . \, (C_{H_2})^2 \, . \, C_{O_2}$.

We may always represent a general chemical reaction between the substances A, A', A'' . . ., apart from questions of energy, by the following equation:

$$n_1 A + n_1' A' + n_1'' A'' + \ldots . = n_2 B + n_2' B' + n_2'' B'' + \ldots .$$

and the velocity will be expressed by: $v = k_1 (C_A)^{n_1} \, . \, (C_A')^{n_1'} . (C_A'')^{n_1''} \ldots .$

If we call $(C)^n$ the *active mass* or concentration of the given substance and suppose it to be equal to 1 in the preceding equation, then v becomes k. Thus, k would be the velocity of reaction in the case in which the product of the active masses or of the single concentrations would be 1.

In the case of reversible reactions, equilibrium occurs when the velocity of reaction, v, of a system is equal to the velocity, v', of the system which represents the opposite reaction, that is, $v = v'$, or:

$$k_1 \, . \, (C_A)^{n_1} \, . \, (C_{A'})^{n_1'} \, . \, (C_{A''})^{n_1''} \ldots . = k_2 (C_B)^{n_2} . (C_{B'})^{n_2'} \, . \, (C_{B''})^{n_2''}$$

and thus:

$$\frac{(C_B)^{n_2} \, . \, (C_{B'})^{n_2'} \, . \, (C_{B''})^{n_2''} \ldots .}{(C_A)^{n_1} \, . \, (C_{A'})^{n_1'} \, . \, (C_{A''})^{n_1''} \ldots .} = \frac{k_1}{k_2} = K,$$

the logarithmic solution of which becomes $\Sigma n_2 \log C_2 - \Sigma n_1 \log C_1 = \log k_1 - \log k_2$. On combining the first members we have the following general, simpler expression: $\Sigma n \log C = \log K$, at which we may also arrive from thermodynamical considerations; in each case K represents the constant of the *law of mass* or of the *isothermic equilibrium*.

We are now able, without penetrating into the mystery of the intimate nature of matter and without, therefore, being able actually to define the affinity of substances, to represent mathematically their behaviour in all their varied transformations by making use of this general equation of the law of mass.

From this equation we see at once that if the concentration of one of the reacting bodies increases, for example, C_A, then the concentration of the reaction product, for example, C_B, must also increase, whilst K remains constant.

Thus the action of the mass is mathematically regulated, the equilibrium of chemical reactions depending upon the concentrations of the reacting substances, that is, upon the relative quantities contained in unit of volume and not on the absolute quantities present in the system.

In the case of the reaction between $H_2 + I_2$, we have seen that a limit is reached in the direction of the reaction $H_2 + I_2 \rightarrow 2HI$, when at 440° about four-fifths of the molecules of H_2 and I_2 are transformed into HI, and that for any given temperature equilibrium of the homogeneous system (all gases) occurs when the molecules H_2, I_2, and 2HI are present in definite proportions. If, however, we now use a chemical reagent to fix the HI so as to separate it in the solid or liquid state, then the equilibrium ceases to exist and further molecules of H and I are transformed into HI in order to re-establish the equilibrium. We may also transform more than four-fifths of the H and I into HI, by displacing the equilibrium in another way, namely, by introducing into the same volume which contains the molecules of the preceding system, say, double the number of molecules of hydrogen (that is, by increasing the concentration of the hydrogen per unit of volume); the probability that molecules of H_2 will encounter those of I_2 then becomes double, and thus the limit of the reaction will be advanced, whilst the velocity of the reaction will remain unaltered under the new conditions.

On applying the general formula of the law of mass to the reversible reaction, $H_2 + I_2 \rightleftarrows 2HI$, we have $K = \frac{(C_{HI})^2}{(C_{H_2}) \cdot (C_{I_2})}$, and thus we see that by increasing the concentration of the hydrogen or of the iodine, we must increase the quantity of HI, since the value of K remains constant.

In the study of chemical equilibria we may distinguish *monomolecular* and *dimolecular reactions*. In the case of hydriodic acid: if this is dissociated under the action of sunlight, the action is monomolecular, $HI = H + I$, whilst if it dissociates under the action of heat, the reaction becomes dimolecular, $2HI = H_2 + I_2$. In many dimolecular reactions the reacting molecules are different from one another. In the case of monomolecular reactions, the velocity of reaction is proportional to the quantity of undecomposed substance, and if the number of molecules of the substance A at the beginning of the reaction is indicated by a, and the number of molecules decomposed in a very short time t by z, we find that the velocity of reaction $\frac{dz}{dt} = k(a - z)$, where k represents the reaction constant.

With dimolecular reactions, we have a molecules of the substance A and b molecules of the substance B, and after a very short time the numbers of molecules which have reacted will be $(a - z)$ and $(b - z)$, so that we arrive at the equation:

$$\frac{dz}{dt} = k_1 (a - z)(b - z),$$

where k_1 is the new reaction constant. In the case of a dimolecular reaction occurring between similar molecules, for example, $2HI = I_2 + H_2$, a becomes equal to b, and the equation takes the form: $\frac{dz}{dt} = k_1 (a - z)^2$.

By means of this equation it becomes possible to discover whether a reaction is monomolecular or dimolecular. On integrating the equation and solving for values of k and k_1, the results obtained are:

$$k = \frac{1}{t} \log \frac{a}{a - z} \text{ and } k_1 = \frac{1}{t} \frac{z}{a(a - z)}.$$

Thus, by bringing about a given reaction in successive measured times and determining the quantities of matter dissociated in a given time, it is possible, by trying to apply one or other equation, to establish whether the reaction is monomolecular or dimolecular.

With the inverse reaction for hydrogen iodide, that is, its formation from hydrogen and iodine on heating, $H_2 + I_2 = 2HI$, if z be the number of the molecules which are dissociated, there will result $\frac{z}{2}$ molecules of hydrogen and the same amount of iodine. The reaction being dimolecular, the reaction velocity will be $k_2 . \left(\frac{z}{2}\right)^2$ and for the general reversible reaction $H_2 + I_2 \rightleftarrows 2HI$, we shall have chemical equilibrium when the two reaction velocities in contrary senses are equal:

$$k_1 (a - z)^2 = k_2 \left(\frac{z}{2}\right)^2 \quad \text{or} \quad \left(\frac{z}{a - z}\right)^2 = \frac{4\,k_1}{k_2} = K.$$

Thus, when equilibrium is established, no matter what the concentrations and temperatures, the ratio between the squares of the quantities of dissociated and non-dissociated substance remains constant.

We have already noted that the *velocity of reaction* depends on the nature of the reacting substances and on their concentration, but we have also noted the influence exerted by the temperature. Rise of the latter increases the velocity of the molecules, and thus the number of their mutual impacts, the reaction velocity consequently increasing. Van't Hoff has deduced experimentally for many substances the ratio between the reaction velocities k_{t_1} and k_t for temperature differences $(t_1 - t) =$ about 10°, and has found that the value of the ratio is generally between 1·9 and 3·5, so that, on increasing the temperature by 10°, the velocity of reaction is doubled or trebled or, for some chemical processes, increased even further (*see* the considerations stated on p. 65).

CATALYTIC PHENOMENA

Now that we have studied chemical reactions qualitatively and quantitatively and know under what conditions, in what sense, and up to what point they occur, we will turn to an interesting category of phenomena which were known as early as the time of Berzelius and utilised during the last few years in important industrial processes, but which even to-day remain without rigorous and exhaustive explanation.

For many years it has been known that, when left to itself, hydrogen peroxide (H_2O_2) decomposes slightly and very slowly into $H_2O + O$, but Berzelius, Schönbein, and a few others had already noted that on adding very small quantities of subdivided platinum or of manganese dioxide, this decomposition proceeded very rapidly, sometimes causing a tumultuous development of oxygen. The platinum remains unaltered and transforms an indefinite quantity of H_2O_2 into $H_2O + O$. The same phenomenon with H_2O_2 may also be induced by other substances, for example, by pumice-stone, by colloidal metallic solutions (*see below*), by blood or rather by a ferment (enzyme) called catalase contained in it.[1]

The case is the same for hydrogen and oxygen. These two gases do not combine at ordinary temperatures except in imperceptible quantities, and after 120 hours at 450° only 20 per cent. is combined. In presence of very small amounts of platinum sponge, however, the reaction occurs rapidly even at ordinary temperatures with formation of water and without alteration of the platinum. Similarly it has been found that the velocity of reaction also varies notably with simple variation of the vessels in which it is produced. Atmospheric oxygen does not react even on heating with hydrochloric acid gas, but in presence of small quantities of copper sulphate or chloride at about 400° reaction occurs

---

[1] The blood of various animals may be distinguished by the degree of its catalytic action. On pouring 1 c.c. of various kinds of blood into separate quantities of 1 per cent. hydrogen peroxide solution, the following quantities of oxygen in c.c. at 0° and 760 mm. are developed: Human blood, 710 c.c.; apes, 706 c.c.; horse, 288 c.c. (venous) and 438 c.c. (arterial); ox, 136 c.c.; goat, 58 c.c.; pigeon, 4 c.c. The catalysts (catalases) in the blood of various animals vary, but those of man and of the apes are the same (L. van Itallie, 1906).

quickly with formation of chlorine (industrial Deacon process). Sulphur dioxide (SO_2) does not react with the oxygen of the air under ordinary conditions, even on heating, to form sulphur trioxide (SO_3), but in presence of platinised asbestos at 45°, 99 per cent. of the SO_2 is transformed into SO_3 (industrial process for the manufacture of sulphur trioxide).

All these special substances capable of accelerating chemical reactions —which would also take place spontaneously, but with extreme slowness (measurable perhaps only after many years)—without taking any part in the reaction, so that they are found unaltered after having transformed a very large quantity of the substance, were called by Berzelius *catalysts ;* their action is called *catalytic* action, and the phenomenon *catalysis.*

Catalysts are not able to induce reactions which would not occur alone at all, but only to accelerate those which can occur even very slowly, without, however, being able to displace the conditions of equilibrium of a chemical process. If, for instance, at 440° the reaction between $H_2 + I_2$ occurs up to 79 per cent. in the sense of the formation of HI, at lowered or higher temperatures, at which the opposite reaction, that is, the dissociation of HI into H and I, is more marked, the same catalyst will also accelerate this opposite reaction.

At certain temperatures, ammonia and hydrogen chloride unite to give ammonium chloride, but only on condition that a trace of water vapour is present. The opposite reaction, that is, the dissociation of ammonium chloride into NH_3 and HCl, can also occur only at high temperatures in presence of traces of water. In this reaction, as in some others, it is always the water which acts as a catalyst.

It has been supposed that catalytic substances form with the reacting substances very unstable intermediate compounds, and that by the decomposition of these the catalytic substances result anew, together with the true final product of the reaction. In many cases, however, it has not been found possible to demonstrate the formation of such intermediate products, and Ostwald prefers to compare the action of catalysts to that of lubricating oil on a rotating wheel, which turns slowly and with much friction when oil is lacking, but much more rapidly under the same impulse if the axis is lubricated, although the lubricant takes no part in the movement, and is not used up.

Those reactions in which it has been shown that small quantities of the supposed catalyst give rise to unstable intermediate compounds which decompose with great rapidity, such as have been recently proved to exist, even in the case of platinum (which gives very labile oxides), are called *pseudo-catalytic phenomena.*

So-called negative catalysts are also known, these impeding or preventing certain reactions which would otherwise take place easily. In 1898 Bigelow found, for example, that minimal traces of mannitol or of certain other organic substances completely prevented the oxidisation of sodium sulphite by oxygen.

The hypothesis that the catalytic phenomenon depends on intermediate reactions which accelerate the phenomenon compared with the direct reaction, and the practical proof of the existence of intermediate reactions, do not suffice to give a general explanation of catalytic phenomena; it is necessary, on the other hand, to show that under such conditions the intermediate reaction proceeds more rapidly than the direct reaction, and even in that case we are not yet able to explain all catalytic phenomena, especially those which hinder the reaction, because in such cases if a reaction occurs more slowly when it takes place by means of intermediate products, it is natural that it should tend by preference to take place in the direct manner, so that we cannot speak of the catalytic influence of intermediate products if these are not formed

Euler recently propounded the hypothesis that, as the velocity of reaction is dependent on the concentration of the free ions, catalysts must have the property of modifying this concentration. This hypothesis is capable of explaining many reactions, but not the fact that in certain cases, when two catalysts are present simultaneously, the reaction velocity increases in a much greater proportion than would be the case according to the sum of the actions of the individual catalysts.

All substances may, perhaps, be specific catalysts for certain reactions, and perhaps all reactions are more or less catalytic reactions, but a general and positive explanation of catalytic phenomena has not yet been given.

AFFINITY

By affinity is understood the force by means of which the atoms are united with one another in the molecule, but it is not always easy to determine this force in practice. Though it may be possible to obtain sufficiently precise data in such cases as, for example, the dissociation on heating of molecular into atomic iodine $I_2 \longleftrightarrow I + I$, this is not the case in reactions which take place by the initial dissociation of all the reacting molecules into atoms and the subsequent union of these to produce new molecules. The reaction velocity does not serve to measure chemical affinity, because it varies greatly with the temperature and may be notably increased by the presence of a simple catalyst. Berthelot believed it to be possible to measure affinity by the heat developed in a chemical reaction. Although, by the third principle of thermochemistry (*see* p. 62), those reactions take place by preference which give rise to the greatest development of heat, thus corresponding with the maximum work, this is generally true only on condition that the reaction occurs without the intervention of external energy, as otherwise it would not be possible to explain the formation of endothermic compounds, which absorb heat during their formation. We can thus obtain a determination of the affinity only by measuring the change of free energy of combination,[1] that is, the heat and external work developed in the formation of a substance from its components.

This external work may be determined in an isothermic and reversible chemical transformation, bearing in mind the thermochemical law of Hess (p. 63). By establishing the relation which exists between the change of free energy and the temperature, it can be shown by calculations that *the diminution of total energy is equal to the change of free energy only at absolute zero*, since by lowering the temperature of a body from dT down to absolute zero, all the heat contained in it is transformed into other forms of energy[2] (*see* pp. 25 and 54).

The change of free energy in a reaction represents the maximum work which the system can give if all the work is transformed into chemical energy. It is, however, not necessary in practice that all the work should be used in every case. Thus, to take an analogous case: by taking certain precautions we may cool a liquid below its freezing-point without solidification and hence without liberation of the latent heat of fusion, having thus abstracted from the liquid merely the quantity of heat corresponding with its specific

---

[1] The *free energy* of a substance is that part of the total available energy which can be transformed into another form of energy (in our case into heat). The difference between the total and the free energy is the *combined energy*, and the ratio between this and the absolute temperature is called the *entropy* (Clausius), which for every substance becomes larger as its temperature is further removed from absolute zero.

[2] If we denote the work done by A, and the thermal effect by q, we have $A_o = q_o$, and in order to calculate q_o it is sufficient to know the thermal effect, qT, of the reaction at the temperature T and the specific heats of the original system (C_I) and of the final system (C_{II}). We then have $q_T = q_o + (C_I - C_{II})T$. If we assume that the specific heat of the substance is the same at all temperatures, we may consider the change of free energy as a linear function of the absolute temperature. Strictly, however, the specific heat is not independent of the temperature and may be represented by the empirical formula, $C = \alpha + \beta T + \gamma T^2 + \ldots$

heat. Thus, in a chemical system we may so arrange matters that all the heat corresponding with the maximum work is not immediately developed, so that intermediate labile chemical systems are formed.

Ostwald opposed to Berthelot's principle of maximum work the *law of successive reactions*, according to which, if a chemical system be transformed into various others, the less stable systems are first formed (with small changes of free energy, that is, with a minimum evolution of heat) and are successively transformed into systems more and more stable. Metastable equilibria are thus produced which, however, follow the common laws of chemical equilibrium. Thus, by the action of chlorine on a solution of sodium hydroxide, we are able to obtain all the following successive reactions :

$$\overbrace{\mathrm{24NaOH + 12Cl_2}}^{\mathrm{I}} = \overbrace{\underset{\text{sodium hypochlorite}}{\mathrm{12NaOCl}} + \underset{\text{sodium chloride}}{\mathrm{12NaCl}} + \mathrm{(12H_2O)}}^{\mathrm{II}} =$$

$$\overbrace{\underset{\text{sodium chlorate}}{\mathrm{4NaClO_3}} + \mathrm{20NaCl}}^{\mathrm{III}} = \overbrace{\underset{\text{sodium perchlorate}}{\mathrm{3NaClO_4}} + \mathrm{21NaCl}}^{\mathrm{IV}} = \overbrace{\mathrm{24NaCl + 6O_2}}^{\mathrm{V}}$$

The maximum of free energy is contained in System I and the minimum amount in System V. In consequence of these successive reactions, it is possible in practice to prepare hypochlorites, chlorates, and perchlorates, even simultaneously, for example, by electrolytic methods.

SOLUBILITY OF GASES IN LIQUIDS

All gases dissolve in liquids to a greater or less extent. It was found by Henry in 1803 and 1805 (and confirmed by Bunsen and his pupils in 1855) that the quantity by weight of a gas absorbed or dissolved by a given quantity of liquid varies with the natures of the gas and of the liquid, but for a given gas and a given liquid *is proportional to the pressure to which the gas is exposed.* Since the volume of a gas is inversely proportional to the pressure, we may say that a *given quantity of liquid always absorbs the same volume* (not the same weight) *of a gas whatever may be the pressure.* If we call the quantity by weight of gas which is present in unit volume of the gas or of the liquid its concentration, we may then say that the concentration of the dissolved gas is proportional to the concentration of the compressed gas in the space above the liquid, and this proportion or ratio, called the *coefficient of solubility* of the gas, remains constant at all pressures and becomes smaller as the temperature is raised, that is to say, the solubility of gases diminishes with rise of temperature. This law is apparently true only for gases which do not combine chemically with the liquid, and in general for small concentrations and small pressures. But by making use of the phase rule, which will be explained later, we shall be able to include the apparently exceptional gases which are partly combined with the liquid, and we shall see that Henry's law may be considered as a particular case of the phase rule, that is, when the gas in the gaseous and liquid phases has the same molecular weight.

In 1807, Dalton showed that this law is true also for gaseous mixtures, and *that each component of the mixture is absorbed in proportion to the ratio in which it is present in the mixture, or, in other words, in the proportion in which it would be absorbed if the other components of the mixture were not present, and it were present alone in unaltered quantity occupying the whole of the volume,* in which case it would thus be present at a reduced pressure.

If, for example, 100 litres of a gaseous mixture at a pressure of one atmosphere contain 20 litres of carbon dioxide, the pressure due to the carbon dioxide (partial pressure) is

$\frac{20}{100}$, that is, $\frac{1}{5}$ of an atmosphere, and the quantity of carbon dioxide dissolved in the water present in the same vessel as the gas is the same as would be dissolved if the other gases did not exist and the volume of 100 litres were occupied exclusively by the 20 litres of carbon dioxide, in which case this would be present at a pressure of $\frac{1}{5}$ of an atmosphere. If in the 100 litres of the gaseous mixture, 50 litres of carbon dioxide were present at a total pressure of one atmosphere, the pressure of the carbon dioxide would be $\frac{1}{2}$, that is, $\frac{50}{100}$ of an atmosphere, that is, $\frac{1}{2}$ that of the total gaseous pressure. In this case the quantity of carbon dioxide absorbed is the same as would be absorbed if the carbon dioxide alone occupied the same volume at a pressure of $\frac{1}{2}$ atmosphere. In every case, then, the quantity of carbon dioxide absorbed depends upon the partial pressure exerted by this gas in the mixture, and its partial pressure is in the same ratio to the total pressure as the volume of the carbon dioxide is to the total volume of the gaseous mixture. Practical illustrations of this law will be found in the chapters on the industries of liquid carbon dioxide, catalytic sulphur trioxide, etc.

Further, it has been shown that the partial pressure of one of the gaseous components of a binary mixture is equal to the vapour pressure of that component in the liquid state, multiplied by its molecular fraction in the binary mixture. According to Dolezalek (1910) this holds also for solutions of gases in liquids. Divergence from this law indicates molecular association or condensation.

Dalton believed that the absorption of gases occurred because their particles entered into the intermolecular spaces of the liquid, and this view was in harmony with the fact that the absorption is proportional to the pressure. In this case, however, different gases should be absorbed to the same amount by the same liquid, which is not the fact; but the hypothesis becomes still more absurd when one remembers that the absorption becomes less with elevation of the temperature, which increases the intermolecular spaces. To-day, on the other hand, it is supposed that a certain attraction takes place between the molecules of a gas and those of a liquid by means of which the particles of gas are at first partially drawn into the liquid, that these attracted gas particles are in turn detached from the liquid surface and that equilibrium and saturation are established when the number of gas molecules attracted by the liquid is equal to the number which are detached in the same period of time in virtue of the kinetic energy which they possess, that is, when the gas is at the same pressure in the liquid as above it. The law of Henry is more rigorously explained by means of the phase rule and of mathematical expressions of the equilibria of various chemical systems, as will be shown later.

Bunsen determined the coefficient of absorption of gases by liquids, that is, the volumes of gas, reduced to 0° and to normal pressure, absorbed by unit volume of the liquid under normal pressure.

All gases dissolve with evolution of more or less heat, and the solubility for a given gas is diminished when a solid substance is dissolved in the liquid.

Certain irregularities shown by certain gases at low temperatures disappear at higher temperatures. It has also been observed that, when the pressure on the gas above the liquid is diminished, the total quantity of gas corresponding with Henry's law is not immediately liberated, but that a kind of supersaturation continues for some time and is only removed by agitating the liquid or by introducing a porous body containing air in its pores.

The question whether the gas absorbed by a liquid is present as such or in the liquid state has not been settled, and although the gas and the liquid form a homogeneous mixture, the particles of gas appear to retain their gaseous character, provided that the temperature does not fall below the critical temperature of any individual gas, in which case the liquefaction of the gas would have to be admitted.

SOLUBILITY OF GASES IN SALT SOLUTIONS. This phenomenon has been studied from a biological standpoint in order to see in what manner carbon dioxide and oxygen are absorbed by the blood, which may be considered as an aqueous solution of various salts, more particularly of sodium chloride. This work has been carried out more especially by Fernet (1858), Heidenhaim, and L. Meyer (1857–1863).

When a chemical reaction occurs between the salt and the gas, Henry's law cannot be applied, but it holds in other cases. The fact that the eagle is able to live even in very high atmospheric regions where the air is rarefied, is due to the oxygen being held chemically and thus not according to Henry's law.

MATTER IN THE LIQUID STATE

Whereas the volume of a gas varies proportionately and without limit with increase or diminution of pressure, the volume of a liquid varies only to a limited extent to a certain constant value.

Liquids, like gases, consist of very mobile particles which transmit pressure in all directions and adapt themselves completely to the form of the containing vessel. Whilst the attraction between the molecules of a gas is almost non-existent, in a liquid this attraction overcomes the kinetic energy of molecular motion and the molecules of a liquid are thus unable to escape; they are, however, not firmly united to one another but travel over one another, the distance between individual molecules remaining constant, even though they travel about in this manner. Thus in liquids an indifferent equilibrium is established between the molecules.

Liquids are compressible to a minimal degree, but, as has been shown by the work of Amagat (1886) and also of Pagliani and Vicentini (1883), they do not follow regular laws as do gases with regard to temperature and pressure.

The *specific gravity* or density of a liquid is given by the ratio between the weight of a given volume of the liquid and that of an equal volume of water, measured at a temperature of 4° (maximum density of water), or more simply the specific gravity (S) is the ratio between the weight (P) and the volume (V) of the liquid (because the volume expressed in c.c. also expresses the weight in grams of an equal volume of water): $\frac{P}{V} = S$. Since it is not convenient to work at a temperature of 4°, there is a general agreement to determine the specific gravity at the temperature 15° referred to water at 4° as unity, these conditions being indicated by placing $\left(\frac{15^\circ}{4^\circ}\right)$ at the side of the specific gravity. The reciprocal value of the specific gravity is called the *specific volume* (w) $\left(\text{thus } \frac{V}{P} = w\right)$, and indicates the volume occupied by unit weight of the given liquid.

The specific gravity is commonly determined with pyknometers, hydrometers, or the Mohr-Westphal balance.

PYKNOMETERS. These are of various types. The simplest is that of Stohmann, and is formed of a glass flask of any size from 25 to 300 c.c., closed by a ground stopper, which is traversed by a capillary tube. The dry apparatus is weighed to at least the nearest milligram ($= P$) and then filled with distilled water at 15°, the stopper being inserted and the excess of liquid thus displaced and the capillary tube left full. The pyknometer is then well dried externally and accurately weighed ($= P'$). It is then emptied, dried in an oven, or more quickly by washing out with a little alcohol and afterwards with ether, and is next filled in the same manner with the liquid under examination at the temperature of 15°. It is again dried outside and exactly weighed ($= P''$). Then $P' - P$ is the weight of the water and $P'' - P$ the weight of an equal volume of the liquid under examination. The specific gravity $S = \frac{P'' - P}{P' - P}$. When greater exactitude is required, this formula must be corrected by comparison with water at 4°, and to weighings *in vacuo*, because the weights P'' and P are smaller than the reality, owing to the displacement by the pyknometer full of liquid of a corresponding volume of air. If we indicate by d the density of water at the temperature t, at which the weighings were made, and by λ the mean weight of 1 c.c. of air (0·0012 gr.), the corrected formula becomes: $S = \frac{P'' - P}{P' - P}(d - \lambda) + \lambda$.[1]

A pyknometer which is very convenient and exact because the temperature of the liquid at any instant is given by means of the included thermometer, is that illustrated in Fig. 20. This is weighed first empty in the usual manner, then filled with water, and then with the liquid under examination, filled up to the mark, *m*, on the capillary tube at the side. If the liquid rises slightly above the mark, it is removed with a small piece of filter-paper.

A simpler and more exact form, particularly for small quantities of liquid, is Sprengel's pyknometer (1873), which consists of a simple U-tube (Fig. 21) with capillary ends, and after being weighed is filled up to the mark, *m*, by sucking up the liquid from the one end as indicated in the right-hand portion of the figure.

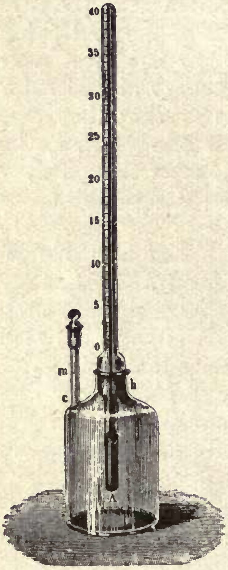


FIG. 20.

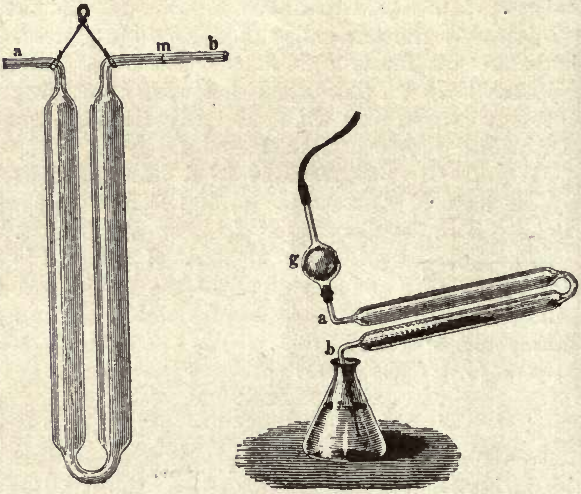


FIG. 21.

MOHR'S BALANCE (1853), *modified by Westphal* (Fig. 22), is based on the *principle of Archimedes*, according to which a body immersed in a liquid apparently loses weight, that is, is impelled upwards, by an amount equal to the weight of the water displaced. If a glass body of constant volume is suspended by a very thin platinum wire and weighed first in the air, then when immersed in distilled water at 15°, and again when totally immersed (that is, up to the same point on the wire) in another liquid, of which the specific gravity is to be determined, the diminutions of weight found when immersed in water and in the liquid under examination indicate the weights of equal volumes of the two liquids; the ratio between these two weights gives the specific gravity.

In practice the work is carried out in the following manner. The glass body provided

---

[1] SPECIFIC GRAVITY OF WATER AT VARIOUS TEMPERATURES

Temperature	Specific gravity	Temperature	Specific gravity	Temperature	Specific gravity
0°	0·999 87	15°	0·999 12	30°	0·995 67
2°	0·999 97	16°	0·998 97	40°	0·992 24
4°	1·000 00	18°	0·998 62	50°	0·988 07
6°	0·999 97	20°	0·998 23	60°	0·983 24
8°	0·999 88	22°	0·997 80	70°	0·977 81
10°	0·999 73	24°	0·997 32	80°	0·971 83
12°	0·999 53	26°	0·996 81	90°	0·965 34
14°	0·999 27	28°	0·996 26	100°	0·958 38

with a thermometer is first hung on the hook at the right-hand end of the beam of the balance, this being then adjusted horizontally by turning the screw, *S*, until the two points at *K* are in horizontal alignment. We have thus equilibrium in the air. When the glass body is immersed in distilled water at 15° it is necessary to hang the rider, *A′*, on the beam in order to bring it back to a horizontal position, as is seen in the figure, and thus we have the weight of water = 1. If, on the other hand, we immerse the glass body in a liquid heavier than water, then, in order to bring the beam to the same zero point, we must place other weights on the beam (the weights, *A*, *B*, *C*, give the first, second, and third decimals respectively), as may be clearly seen from the two examples in Fig. 23. In the case of liquids lighter than water, the weight A_1 must be removed, and thus we have the arrangement illustrated in the same Fig. 23 to the right. We may even estimate the fourth decimal figure approximately if the weight *C* is placed on the beam between one division and the next. If the specific gravity at 15° is to be referred to water at 4°, it is necessary to multiply by 0·99912 (specific gravity of water at 15°, *see* the Table on p. 76).

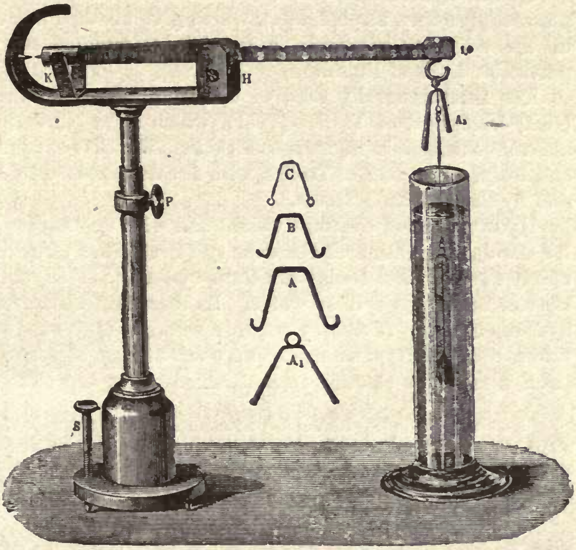


Fig 22.

HYDROMETERS. Hydrometers are much used in commerce and also industrially, and their discovery was due to the philosopher Hypatia of Alexandria, about the year 400. There are hydrometers of constant volume (Nicholson) and hydrometers of constant weight, the latter being the more commonly used.

Their employment for the determination of the specific gravity of liquids is based on the fact that a floating body of constant weight and of stable form, if immersed in a liquid, will displace a weight of the latter equal to its own. Hydrometers are ordinarily formed of small glass cylinders suitably graduated and weighted below by means of mercury or lead shot so that they float in a vertical position when immersed in the liquid (*see below*, figure of Baumé's hydrometer.) The thinner the stem the more exact are the readings. For accurate determinations the scale is read by slowly immersing the dry hydrometer in the liquid in such a way that it is not wetted above the graduation corresponding with the correct specific gravity, or the liquid is poured carefully into the cylinder containing the hydrometer, in such a manner that the part of the stem remaining above the liquid is not moistened (if the stem of the hydrometer above the liquid is wetted, the instrument weighs more and the reading is inexact).

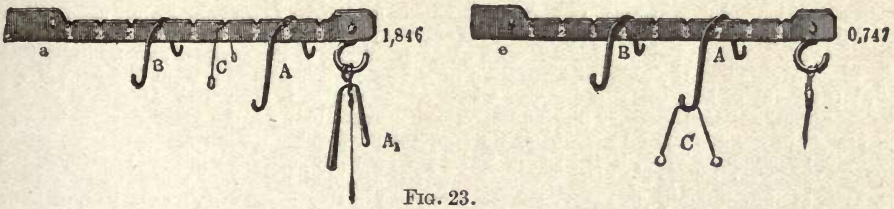


Fig. 23.

Hydrometers are constructed for liquids heavier than water and for liquids lighter than water, and the scale is either *rational*—when the indications are in direct accordance with the specific gravity (centesimal hydrometer of Gay-Lussac)—or *empirical*, in which case the specific gravity has to be deduced from corresponding tables (hydrometers of Baumé, Beck, etc.) or calculated from formulæ. They are called densimeters when the specific gravity is indicated directly on the scale.

Gay-Lussac's centesimal hydrometer gives the specific gravity of a liquid heavier or lighter than water by dividing 100 by the figure given on the stem at the point up to which it sinks.[1]

Special hydrometers are also constructed for particular liquids or solutions (sugar, glucose, glycerine, alcohol, etc.), which give on the scale direct readings of the percentage of the dissolved substance, a special hydrometer being obviously required for each particular kind of liquid.

The most generally used of these are the centesimal alcoholometers of Gay-Lussac (1820–1824) and of Tralles (1811), which show directly the percentage by volume of alcohol contained in aqueous solutions. The first is commonly used in France, Austria, and Italy, whilst that of Tralles, with a scale corrected by Brix, is officially used in Germany and by the Italian Customs.[2]

Hydrometers of constant weight and with an empirical scale are much used in practice for the determination of the density of solutions of acids, salts, etc., and the most commonly used of these to-day are those of Baumé (1768) and of Beck (1803), both for liquids heavier and lighter than water. In recording observations indicating degrees of these hydrometers it is necessary to state whether they refer to liquids lighter or heavier than water, because the same figures may refer to the one or to the other (Fig. 24). The graduation is made by starting from distilled water and from a salt solution of known specific

---

[1] The scale of Gay-Lussac's centesimal hydrometer is calibrated by immersing the instrument, the tubular stem of which is open at the top, in distilled water at 15° and weighting it with mercury to such an extent that it floats with about half the length of the stem immersed; this point is called 100°. The weight of water displaced at this moment is given by the weight of the glass apparatus r plus the weight of the mercury p. If we then add still more mercury p' to the hydrometer so that $r + p' = 2\,(r + p)$, we shall have to indicate the point to which it sinks by 200°, because the volume or weight of water displaced will be doubled. The open end of the stem is then sealed in a blow-pipe. On dividing the space between 100 and 200 into 100 parts, and also continuing the divisions in the opposite direction, that is, below the 100° mark, we obtain a scale which will give the specific gravities of liquids heavier or lighter than water. If, for example, we immerse the hydrometer in a liquid which indicates 80°, we are able to say that the displaced liquid (80 parts by volume) weighs as much as 100 parts of water, because the weight of the hydrometer is constant; and if we indicate the weight of 1 part of water by 1, an equal volume of the liquid under consideration (that is, its specific gravity) will be $\frac{100}{80} = 1{\cdot}25$. If the hydrometer floats in another liquid up to the 120° mark, the specific gravity of this liquid will be $\frac{100}{120} = 0{\cdot}833$. In general the specific gravities of liquids, lighter or heavier than water, are deduced from the readings of Gay-Lussac's hydrometer, by dividing 100 by the degree indicated on the scale. In practice, in order to avoid the use of hydrometers with a very long scale, separate instruments are made for liquids heavier or lighter than water.

[2] The scale of centesimal alcoholometers is graduated by immersing the instrument in various solutions of alcohol and water prepared with exact quantities of the components and indicating by 100° on the stem the point of immersion in absolute alcohol and by 0° at the base of the stem the point of immersion in distilled water. Each degree is then fixed by means of the corresponding solution, because no simple proportion exists between the volumes of water and of alcohol in the mixture on account of the contraction of volume (accompanied by evolution of heat) on mixing. Thus, if 460 c.c. of water are added to 500 c.c. of absolute alcohol, the volume of the mixture is only 930 c.c. instead of 960 c.c., and 100 c.c. of this mixture contain 53·7 c.c. of pure alcohol. The alcoholometer immersed in this liquid will give the reading 53·7. The differences between Tralles' and Gay-Lussac's degrees are small, and are due to the fact that Tralles determined the specific gravity of the alcoholic solutions at the normal temperature of 15·56° C. (= 60° F.), and then referred these to equal volumes of water at 4°; according to the corrections of Brix (officially used in Germany and also by the Italian Customs for alcohol), the specific gravity is referred to that of water at the same temperature of 15·56°. Gay-Lussac's degrees, on the other hand, refer to the temperature of 15° and to water at 15°. Strictly speaking, the true specific gravity is found neither in the one case nor in the other, because 1 c.c. of water at 15° weighs 0·99912 gr., and Fischern (1872) prepared corrected tables by multiplying the centesimal degrees by 0·99912, but these have not come into use in industrial practice.

Richter in Germany and Lejeune in France (1872) prepared centesimal alcoholometers which gave the direct percentage weights of alcohol, but these have not met with general acceptance.

It need hardly be pointed out that alcoholometers can be used only for mixtures of alcohol and water and not for alcoholic liquids such as wine, beer, and spirits, in which other substances are present which influence the specific gravity.

gravity (*see* note below). The specific gravity is obtained from the readings of these hydrometers by means of tables or very simple formulæ. The relationship between Baumé degrees (abbreviated Bé.) for liquids heavier than water will be found in a later table in the chapter on sulphuric acid, and for liquids lighter than water in the chapter on Ammonia.[1]

The boiling-point, evaporation, distillation, etc., are very important in connection with the study of liquids, but we shall not consider here the laws of heat and the optical phenomena in their relation with liquids in connection with the study of organic substances (Vol. II., "Organic Chemistry").

We shall merely mention that while gases give spectra containing well-marked luminous lines, the corresponding liquids, on the other hand, give continuous spectra, which, however, contain dark lines in place of the luminous lines of the corresponding gas. Hence, as the gas gradually approaches the liquid state the characteristic luminous lines of its spectrum become enlarged until they coalesce, giving a complete spectrum containing dark absorption bands.

The behaviour of polarised light passing through liquids is also characteristic of certain substances. It forms an extensive and important branch of physical chemistry which is of special importance for organic substances, and will be studied in the second volume of this work.

The capillary phenomena of liquids are in a certain relation with their chemical composition, but no sufficiently general laws have yet been found to justify the deduction of valuable results.

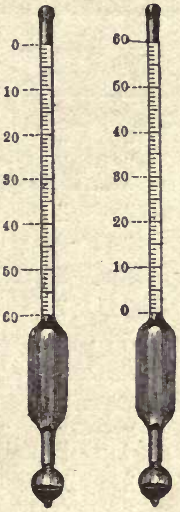


FIG. 24.

We shall encounter important laws on studying the solutions of salts or other substances in liquids, and with their help shall arrive at new and simple methods for determining the molecular weights of many substances, even of such as cannot be converted into vapour.

---

[1] The scale of Baumé's hydrometers for liquids lighter than water is obtained by indicating by the point 0° the immersion-point at the lower end of the stem when the hydrometer is immersed in a solution of 90 parts of water and 10 parts of sodium chloride, at the temperature of 17·5°, and by 10° the immersion-point in distilled water at the same temperature. The space from 0°–10° is divided into 10 equal parts and then continued up to the top of the stem, and this gives the maximum number of degrees for lighter liquids. In the scale of the hydrometer for liquids heavier than water, the immersion-point in distilled water is indicated by 0° at the top of the stem, and the immersion-point in a solution produced from 85 parts by weight of water and 15 parts of sodium chloride at a temperature of 17·5° is taken as 15°. The space between 0° and 15° is divided into 15 parts, and these divisions are continued down the stem as far as about 70°. With the first hydrometer water is indicated by 10° and with the second by 0°, and thus it is always necessary to indicate to which of these two hydrometers the degrees Bé. refer.

In Beck's hydrometer, on the other hand, the zero-point at about the middle of the stem indicates the specific gravity of distilled water at a temperature of 12·5° and 30° the point of immersion in a solution the specific gravity of which is 0·850. The space from 0° to 30° is divided into 30 parts, and the same divisions are continued both above and below the zero-point. Here also, if it is not clearly expressed, the same degree may refer to a liquid lighter or heavier than water.

In order to reduce the degrees (n) of these hydrometers to the corresponding specific gravity (S), the following formulæ may be used. For rational Bé. hydrometers for liquids heavier than water, $S = \frac{144{\cdot}3}{144{\cdot}3 - n}$, and for those lighter than water, $S = \frac{144{\cdot}3}{134{\cdot}3 + n}$; in Beck's hydrometer for liquids heavier than water, $S = \frac{170}{170 - n}$, and for those lighter than water, $S = \frac{170}{170 + n}$.

Very occasionally another hydrometer is used in France for alcoholic liquids and extract, namely, Cartier's hydrometer, which differs very slightly from that of Bé.—the 10° points correspond on the two hydrometers, and 29° Cart. equal 31° Bé.

In England especially, for liquids heavier than water Twaddel's hydrometer (Tw.) is used, and the specific gravity, S, is converted into degree Tw (n) by the formula $n = (S - 1)\ 200$, or *vice versa*. The specific gravity is obtained from degrees Tw. by the formula $S = \frac{n + 200}{200}$. The following relationships exist between degrees Bé. and degrees Tw.; 0° Bé. = 0° Tw., 6° Bé. = 9° Tw., 16° Bé. = 25° Tw., 25° Bé. = 42° Tw., 35° Bé. = 64° Tw., 50° Bé. = 106° Tw., 60° Bé. = 142° Tw., 67° Bé. = 173° Tw.

It is sometimes useful to know the specific heats of liquids or solutions, and we therefore give the following convenient and practical table:

SPECIFIC HEATS OF LIQUID SUBSTANCES AND SOLUTIONS

Substance	Temperature of observation	Specific heat	Substance	Temperature of observation	Specific heat
Ammonia, liquid	0°	0·876	Nitric acid 3·4%	20°–50°	0·962
,, ,,	30°	1·218	Ethyl ether	0°	0·529
,, ,,	70°	1·233	,, ,,	30°	0·547
,, aqueous 3%	18°	0·997	,, ,,	180°	1·041
Potassium hydroxide 39%		0·697	,, alcohol	0°	0·547
,, ,, 8%		0·900	,, ,,	65°	0·699
Sodium ,, 73%	0·98°	0·960	,, ,, 10%	10°–16°	1·015
,, ,, 23%	18°	0·847	,, ,, 50%	0°–15°	0·992
Calcium chloride 41%	23°–80°	0·636	Formic acid	20°–80°	0·517
,, ,, 3%	20°–51°	0·955	Aniline	15°	0·514
Magnesium chloride 26%	22°–52°	0·682	,,	50°	0·529
,, ,, 2·6%	18°–52°	0·959	Benzene C_6H_6	10°	0·407
Sodium ,, 24%	18°	0·791	,,	50°	0·450
,, ,, 5%	19°–46°	0·944	Chloroform	0°	0·232
,, sulphate 30%	24°–100°	0·781	,,	60°	0·238
,, ,, 2%	14°	0·976	Hexane C_6H_{14}	0°–50°	0·527
Calcium nitrate 48%	20°–50°	0·625	Acetic acid	20°–50°	0·512
,, ,, 4·4%	20°–50°	0·951	,, ,, 50%	22°–62°	0·778
Sulphur dioxide, liquid	0°	0·317	Glycerine	15°–50°	0·576
,, ,, ,,	40°	0·342	,, 50%	15°–50°	0·813
,, ,, ,,	155°	2·200	Methyl alcohol	15°–20°	0·601
Sulphuric acid, pure	20°	0·345	,, ,, 20%	7°–11°	1·073
,, ,, ,,	50°	0·359	Nitrobenzene	10°–15°	0·348
,, ,, 50%	5°–22°	0·332	Palmitic acid, liquid	65°–104°	0·653
,, ,, 5%	5°–22°	0·960	Carbon disulphide	30°	0·240
Hydrochloric acid 17%	18°	0·749	,, ,,	80°	0·260
,, ,, 2%	18°	0·965	Petroleum	21°–58°	0·511
Nitric acid 58%	20°–50°	0·655	Olive oil	6°	0·471

STUDY OF DILUTE SOLUTIONS

OSMOTIC PRESSURE. The study of liquids acquires new importance when extended in a special manner to dilute solutions.

About the year 1750 the Abbé Nollet observed that when a beaker filled with spirits is closed by an animal membrane and immersed in water, the membrane swells and sometimes bursts. This observation was forgotten by everybody and was rediscovered by Parrot in 1815, by W. Fischer in 1822, and by Dutrochet in 1827; it was classified as an osmotic phenomenon, and Liebig in 1848 endeavoured to explain by its means the movement of the liquids in the animal organism.

The modern interpretation of this phenomenon is as follows:

If water is poured on to the top of a strong solution of sugar, an internal movement of the liquid at once takes place, and the molecules of sugar pass from the concentrated solution into the superposed liquid until equilibrium is established and the two solutions have the same concentration. If from the first a porous membrane only permeable by water and not by the sugar molecules is placed between the concentrated solution and the layer of water, the sugar molecules which have a tendency to diffuse into the superposed liquid then collide with the membrane, exerting a pressure. Since the phenomenon is an ordinary process of osmosis, this pressure is called *osmotic pressure.*

In 1867 Traube prepared artificial semi-permeable membranes of this kind by means of the films which form at the limiting surface of two superposed solutions, one of copper sulphate and the other of potassium ferrocyanide. In 1877 W. Pfeffer prepared rigid membranes by producing the precipitate of copper ferrocyanide directly in the pores of an unglazed porcelain cell (battery cell). These rigid osmometers, perfected by Naccari in 1898 and provided with a manometer, serve for the study of this important phenomenon of osmotic pressure (Fig. 25).

On placing inside the porous cell of the osmometer a 1 per cent. solution of sugar, and immersing the whole in water, the manometer shows after a short time a pressure of about two-thirds of an atmosphere (49·3 cms. of mercury). If, on the other hand, a 2 per cent. sugar solution is placed in the osmometer, the pressure is doubled, that is, it becomes $1\frac{1}{3}$ atmospheres; with a 3 per cent. sugar solution the pressure is trebled (two atmospheres), and in the same way with a 6 per cent. sugar solution, a pressure six times as great as that obtained with a 1 per cent. solution is obtained.

Various hypotheses have been proposed to explain this interesting behaviour, by van't Hoff (1885–1895), Ostwald (1891–1893), Nernst (1883–1893), Pupin (1889), Bredy (1889), Lothar Meyer (1890), and later by Nasini, Pickering (1890), Boltzmann (1890), Naccari (1893), Magnanini (1894), Moore (1895), and the writer (1895). Some of these authors maintained that the osmotic pressure must be due to the particles of the dissolved substance, whilst the solvent which is able to enter and leave the osmometer freely could not exercise any pressure. Others, on the contrary, held the exactly opposite opinion and regarded the osmotic pressure as due entirely to the solvent. Others, again, accepted neither the one explanation nor the other, but argued that even in open vessels there should be a large osmotic pressure of the solution and that the walls of the vessel ought necessarily to be broken (*Pupin*). These differences of opinion were cleared up later, and it was shown that even in open vessels many properties of solutions are in strict accordance with the osmotic pressure. A logical explanation of osmotic pressure is found in the following argument, which unites the views of all the above-mentioned authors, and also explains the apparent exceptions or abnormalities of osmotic phenomena.

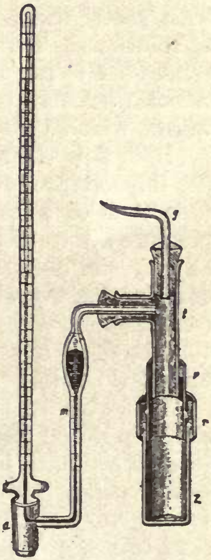


FIG. 25.

We will imagine a Pfeffer osmometer (porcelain cell, etc.), semi-permeable, of one litre capacity and full of a gas, *A*, unable to escape. If we now surround the cell with another gas, *B*, which is able to penetrate into the cell, the manometer will indicate two atmospheres' pressure (one from the gas *A* at ordinary pressure, and one from the gas *B*). If we further suppose the osmometer to be varnished with an ideal substance which has the property of preventing the exit of the internal gases *A* and *B*, but permits the entrance of a third gas, *C*, the manometer will then indicate three atmospheres' pressure.

On varnishing the cell with another ideal substance which permits a fourth gas, *D*, to enter without allowing the first three gases to escape, a pressure of four atmospheres will be indicated. Equilibrium is established for the last gas, *D*, which has free access, when as many molecules enter the osmometer as leave it. In order to understand under what conditions this last gas, *D*, is present in the interior of the osmometer, which indicates a pressure of four atmospheres, although the gas *D* communicates with the outside where the same gas *D* is at one atmosphere pressure only, we may imagine one litre of the gas *D* to be enclosed in an impermeable cylinder provided with a piston, at the ordinary atmospheric pressure. If we now reduce the volume to a quarter by means of the piston, the pressure will become four atmospheres. This gas is now under equal or analogous conditions to the gas *D* contained, together with the other gases, in the osmometer. In fact the difference between the gas *D* in the cylinder at one atmosphere and the same gas in the osmometer at four atmospheres consists in this, that in a given volume, say 1 c.c., four times as many molecules are present, and thus the average distance between the molecules is four times as small.

But in the osmometer, the gas *D* mixing with the other three gases is present under the same conditions, that is, it has only one-quarter of the total space at its disposal, since the other three-quarters are occupied by the other three gases. The distance between the molecules of the various gases taken together is only one-quarter, because in 1 c.c. in the interior of the osmometer the number of the molecules is four times as great as in the gas *D* outside at a pressure of only one atmosphere. We know also that the pressure is due to the number of impacts of the molecules on the walls and also that the gas *D* has free entry and exit and that as many molecules enter as escape. In the interior these molecules collide with other molecules and are not always able to arrive at the pores whence they escape, and the difficulty from this cause is fourfold, because in 1 c.c. four times the number of molecules are present as in 1 c.c. of the external gas. As equal numbers of molecules of the gas *D* are always escaping and entering at a pressure of four atmospheres, the gas *D* inside must of necessity be at four atmospheres' pressure, and thus as only one-fourth of the molecules are in a position to arrive at and collide with the walls in unit of time, they must, therefore, collide four times as many times with the walls because the distance between the molecules is four times smaller, and the possibility must exist to collide more often with the pores through which they escape.

Now, always remembering that the total internal pressure is due to the sum of the partial pressures exerted by the individual gases, it is a logical and justifiable hypothesis that the gas *D* inside is present at four atmospheres' pressure, together with the other gases, whilst outside it is at a pressure of one atmosphere. The same hypothetical experiment which we have made with gases, using the osmometer, will also explain very well the behaviour of solutions. Turning to the sugar solutions of 1 per cent., 2 per cent., 3 per cent. . . . 6 per cent. concentrations, we may very well affirm that the osmotic pressure is due to the sugar molecules, but is exerted by the solvent, water, which penetrates into the interior of the osmometer.

It is now clear that we may consider the osmotic pressure as the sum of the impacts produced by the dissolved substance and by the solvent, and that it is thus of a kinetic nature. The causes of the manifestation of osmotic pressure are to be found in the mechanical combination represented schematically by the osmometer (which may be replaced by a vegetable cell, etc.), a combination constituted in its entirety of molecular particles of various sizes (solvent and dissolved substance) endowed with continuous movement and contained in a semi-permeable receptacle (permeable for the solvent only) and of the solvent which surrounds this receptacle.

Wherever in nature a similar or analogous combination is present, we shall obtain an osmotic pressure. It appears, in fact, that the rise of the sap to extraordinary heights in the most gigantic trees (the height of eucalyptus trees reaches 160 m.) is due to osmotic phenomena which occur between the vessels carrying the sap and the vegetable cells, as was shown by the brilliant experiments of the Dutch botanist de Vries in 1884, and not to capillary phenomena,[1] as was once thought. In 1909 Bigelow and Bartel determined the size of the pores of an unglazed porcelain plate by closing a non-porous vessel with this plate and then compressing water inside until it issued from the pores. From the pressure necessary for this purpose and with the aid of Jurin's law, they calculated the size of the pores. They were thus able to

---

[1] **CAPILLARITY OF SOLUTIONS.** Schönbein noticed that, when the lower end of a vertical strip of filter-paper dips into a solution of hydrochloric acid, the water rises higher up the paper than the acid. Holmgren's investigations on such phenomena from a stoichiometrical standpoint led to a simple formula regulating the ratio between the heights attained by the solvent and by the dissolved acid. The constant in this formula depends on the nature of the absorbent material (gypsum, paper, silk, etc.) and in some cases varies for similar papers of the same origin. The degree of moistness of the air has a considerable influence on the height, so that experiments of this kind are made in an atmosphere saturated with moisture. The temperature and the presence of indifferent, extraneous substances influence the time taken in the rising, but not the final height. Equivalent solutions of strong acids rise to the same height; the weak acids rise still higher, although sulphuric acid and various comparatively feeble benzenesulphonic acids give smaller rises. Bases rise higher than acid solutions of equivalent strengths and weak bases higher than strong ones. Salts undergo partial hydrolysis. Ferrous salts rise higher than ferric salts, but stannous and stannic salts rise equally. Salts of strong bases rise higher than those of weak ones. The capillary rise may possibly be inversely proportional to a factor obtained by multiplying the degree of electrolytic dissociation by the molecular weight.

No general theory of capillary phenomena has yet been established and many points in connection with solutions still wait explanation.

establish that a sugar solution shows the phenomena of osmotic pressure if the porcelain cell of the osmometer has pores of a diameter less than 0·37 μ.

Solutions of different substances of equal concentration by weight produce different osmotic pressures. De Vries, however, succeeded in preparing isotonic solutions, that is, solutions which exerted the same osmotic pressure, by dissolving various quantities of the substances in one and the same quantity of solvent. This procedure led to the important discovery that isotonic solutions are always equimolecular, that is, solutions which contain the various substances dissolved in the proportion of their molecular weights in equal volumes of the solvent and thus contain the same number of molecules, all exert the same osmotic pressure.

This is, however, nothing else but Avogadro's law as enunciated for gases in another form, as according to this law equal volumes of different gases under the same conditions of temperature and pressure contain equal numbers of molecules, the weights of these gases being in the same ratio as their respective molecular weights (*see below*, the demonstration of the relation which exists between osmotic pressure and the pressure of gases).

It is thus evident that osmotic pressure gives us a method of determining the molecular weights of substances. In fact, if the osmotic pressure exerted by a solution containing the molecular weight in grams of a known substance in a given volume is known, and if we then dilute or concentrate solutions of substances of unknown molecular weights in the same solvent until they exert the same osmotic pressure, we shall know that equal volumes of these solutions contain the same number of molecules as are contained in the same volume of the solution of the known substance.

For his determinations de Vries used vegetable cells which he immersed in solutions of various concentrations, and thus obtained at will various osmotic pressures. The cells of *Tradescantia discolor* and *Curcuma rubricaulis*, and even *blood corpuscles* (Hamburger), are well suited for this purpose. It may be seen under the microscope that if these cells are immersed in a saline solution more concentrated than the protoplasmic liquid, the hyaloplasm contracts. If, on the other hand, the saline solution is more dilute, the cell swells until its envelope sometimes even bursts. This phenomenon, called plasmolysis, was used by de Vries to determine the molecular weights of various substances.

In 1887 van't Hoff showed that isotonic (equimolecular) solutions remain isotonic even if the temperature is varied, and that the osmotic pressure is proportional to the absolute temperature. Thus, to such isotonic solutions, when very dilute,[1] the general formula expressing the laws of Boyle and Gay-Lussac may be applied, namely, $PV = RT$.

For all gases the constant R is equal to 84,770 (that is, $R = \frac{PV}{T}$, *see* p. 26).

If in place of P in this formula we introduce the osmotic pressure of a 1 per cent. sugar solution at 0° (273° absolute), that is, the pressure of a column of mercury of 49·3 cms. [equivalent to 671 grs. $= 49{\cdot}3 \times 13{\cdot}6$ (weight of 1 c.c. of mercury)] as was found by Pfeffer, the molecular weight of sugar expressed in grams (342) at 1 per cent. dilution will occupy a volume, V, of 34,200 c.c. and the formula will become :

$$R = \frac{671 \times 34200}{273} = 84100.$$

Thus we see that the constant, R, deduced from the osmotic pressure may be considered equal to the gas constant, and that, in fact, the quantity of sugar in solution, if it could be transformed into a gas, would exercise a pressure equal to the osmotic pressure of that solution.

---

[1] We make the reservation that the solutions must be very dilute, because this law has also a limitation and is only true for great dilutions, just as the law for gases and vapours is only true when these are studied at temperatures far from their point of condensation.

We may thus visualise this action of the solvent by supposing it to assist in the separation of the sugar molecules from one another by carrying them to such a distance apart that the same quantity of sugar will be found as would be present in the same volume of vapour if the solvent were absent. Again, if we take one litre of alcohol vapour, weighing about 1½ grms., the molecules are at a certain distance from one another, this distance being characteristic of alcohol in the gaseous condition. If we now take another 1½ grms. of alcohol, that is, the same number of molecules of alcohol as before, and dissolve them in a litre of water, the molecules of alcohol will be present at the same distance from one another as was the case in the gaseous state; and we may say in general that, with dilute solutions, the solvents produce a species of gasification of liquid and solid substances (as had already been suggested by Rosenstiehl in 1870).

The determination of molecular weights by means of osmotic pressure is very suitable for all indifferent substances, but gives abnormal results in the case of acids, bases, and salts, especially if these are dissolved in water. We shall see below how these exceptions, which are due to the dissociation of the dissolved molecules, have been brilliantly explained.

SURFACE TENSION OF LIQUIDS. At their surface, liquids contain a layer of molecules which are present under different conditions from those in the interior of the mass, and give rise to various phenomena capable of provisional explanation by the following hypothesis. In the interior of a liquid the molecules are present in equilibrium, because they collide with one another in several directions (from above, from below, and from the sides), and there must therefore be an enormous latent internal pressure due to the impacts between the molecules of the liquid. This pressure is balanced by the attraction between the same liquid molecules. The molecules at the surface receive impacts only from the molecules below and to a certain extent from the sides, but not from above, and if they do not evaporate it is because of the molecular attraction by the molecules below (Fig. 26). These surface molecules are, however, transformed into vapour with about half as much work as the others, and therefore have a tendency to escape from the liquid with great facility, forming vapour. In any case they possess certain properties which are manifested in various ways.

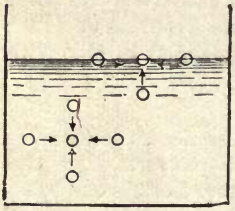


FIG. 26.

This force at the surface of liquids shows itself as a tendency to diminish their surface area, and thus as a tendency to assume a spherical form, concave when the liquid moistens the walls of the receptacle and convex when it does not moisten them. These special forces act on the surface as though the liquid itself were enclosed in a stretched elastic film which tended to contract.[1] In capillary phenomena this surface tension of liquids manifests itself by the rise of a column of the liquid in a capillary tube, the upward movement continuing until the weight of the liquid column is in equilibrium with the surface tension. Mendeléev (1860), Quincke and Duclaux, Stephan (1886), and specially R. Schiff (1884), found that certain stoichiometric relations may be deduced between various substances, but they were not able to deduce a general law, although for certain groups of substances the rise of the liquids in capillary tubes is the same for equal molecular weights (for example, with isobutyl alcohol, ether, etc.).

---

[1] Thus, if from the clean-ground end of the glass tube of a pipette held horizontally drops of a liquid are allowed to form, these assume a spherical form in falling; also if a drop of a liquid is removed from the action of gravity by being dropped into another liquid of the same density with which it does not mix, instead of extending on the liquid surface, it contracts and forms a floating spherical drop. Similarly, when mercury is thrown on to a flat solid it collects into small spherical drops by virtue of its surface tension.

VAPOUR PRESSURES OF SOLUTIONS AND MOLECULAR WEIGHTS

Water boils and is transformed into steam when its vapour pressure is equal to the atmospheric pressure. Water containing a salt in solution boils at a higher temperature, the vapour pressure being diminished by an amount which becomes greater as the amount of salt in solution increases; the rise in the boiling-point is proportional to the diminution of the vapour pressure of the solution.

This fact, although noted by Faraday (1822), by Griffith (1824), and by Legrand (1835), was first methodically studied by Gay-Lussac and then by von Babo in 1849–1857, and Wüllner in 1856–1860; it was then found that the diminution of the pressure is the same at whatever temperature the experiments are conducted.

The diminution of the vapour pressure produced by 1 gram of various substances in the solvent water was then determined.

In 1883–1884, Ostwald suggested that the diminution of the vapour pressure should be referred to a weight of the substance representing the molecular weight, and that the diminution of the molecular pressure would then have a constant value. In 1885 Tammann showed experimentally that the molecular decrease of the vapour pressure is the same for analogous salts dissolved in water, but notable differences were found in the case of different salts.

In 1886 Raoult made numerous experiments in the barometric vacuum, employing other solvents than water, and obtained results of very wide and general bearing which fully confirmed the prophecy of Ostwald (1883). We have thus at our disposal another very convenient method of determining the molecular weights of a very large number of substances, simply by observing the decrease in the vapour pressure of the solvents on dissolving such substances, that is, by determining their boiling-points. This law also is true only for very dilute solutions.

If we denote the vapour pressure of the solvent by f and that of the solution of g grams of the substance by f', then $f - f'$ indicates the *absolute decrease* of the vapour pressure, whilst $\frac{f-f'}{f}$ indicates the *relative decrease* which, as was shown experimentally by Raoult in 1886, remains constant at all temperatures. If we then indicate by k a constant which represents the relative decrease for concentrations of 1 gram of substance per unit volume, we shall have for g grams:

$$\frac{f-f'}{f} = k \,.\, g.$$

We know that *equimolecular solutions have equal vapour pressures*, that is to say, the molecular lowering of the vapour pressures of various substances dissolved in the same solvent is a constant quantity, or in order to obtain an equal decrease of the vapour pressure it is necessary that a given quantity of a dissolved substance should be dissolved in quantities of different solvents which are in the same proportion to one another as the respective molecular weights of these substances. Hence the lowering of the vapour pressure is independent of the nature of the solvent and of the dissolved substance, and is a function only of the numbers of molecules of the solvent (N) and of the substance (n) only. The ratio between the vapour pressure of the solution and that of the solvent is the same as that between the number of the molecules of the solvent (N) and the number of molecules of the solution, $N + n$, that is, $\frac{f'}{f} = \frac{N}{N+n}$, and as the relative decrease of the vapour pressure of a solution corresponds with the relative number of molecules of the dissolved substance $\frac{n}{N+n}$, we have: $\frac{f-f'}{f} = \frac{n}{N+n}$, so that the relative decrease of the vapour pressure of a solution is equal to the ratio between the number of molecules of the dissolved substance and the total number of molecules in the solution. Since, however, we do not in practice know the absolute number of the molecules, we must introduce into this formula the corresponding relative number, which can always be easily found by dividing the weights of the substance (g) and solvent (G) by the corresponding molecular weights (m and M), so that $\frac{g}{m} = n$ and $\frac{G}{M} = N$; on substituting these known values in the preceding general formula, and taking, for simplicity's sake, a quantity of solvent in grams expressed by the molecular weight (so that $N = 1$), we obtain the formula :

$$\frac{f-f'}{f} = \frac{\frac{g}{m}}{1+\frac{g}{m}} = \frac{g}{g+m}.$$

or inversely : $\frac{f}{f-f'} = \frac{g+m}{g}$, from which :

$$m = \frac{fg}{f-f'} - g = \frac{fg}{f-f'} - g\left(\frac{f-f'}{f-f'}\right) = \frac{f'g}{f-f'}$$

By means of this general formula, $m = \frac{f'g}{f-f'}$, we can always determine the molecular weight of any substance.

Let us take an example : 11·346 grams of turpentine oil were dissolved in 100 grams of ether. Before the addition of the turpentine, the vapour pressure, f, of the ether was 38·30 cms. of mercury, whilst that of the solution, f', was 36·1 cms., and thus $f - f' = 2·29$. We must now refer the weight of the dissolved substance, not to 100 grams of ether, but to the number of grams indicated by the molecular weight of ether (= 74); the value, g, will be obtained from the following proportion : $100 : 11·346 = 74 : g$, so that $g = 8·396$. On introducing this value into the general formula, we have : $m = \frac{8·396 \times 36·1}{2·29} = 132$, this value being very close to the theoretical molecular weight, which is 138.

EBULLIOSCOPIC METHOD OF DETERMINING MOLECULAR WEIGHTS. It is not convenient in practice to determine the vapour pressures of various solvents and solutions at the same temperature, while it is much easier to determine at which temperature the solution and the solvent have the same vapour pressure. The atmospheric pressure is taken as the constant vapour pressure; the solvents and the solutions will then have the same vapour pressure when they overcome the atmospheric pressure, that is, when they boil. In this case the temperatures are given by the boiling-points of the solvent and solution.

Raoult had already shown that the diminution of vapour pressure of a solution, compared with that of the solvent, is proportional to the rise of its boiling-point, also compared with that of the solvent, so that in calculating the molecular weight from the diminution of vapour pressure we may substitute for this the rise of boiling-point.

From the general formula $\frac{f-f'}{f} = \frac{n}{N+n}$, we may deduce that for a solution formed from 99 gram-molecules of solvent and 1 gram-molecule of the substance, the depression of the vapour pressure of the solvent is equal to one-hundredth of the ordinary pressure, with which a certain rise of the boiling-point of the solvent corresponds, and if this rise, due to 1 mol., is multiplied by 100, we obtain the so-called molecular elevation of the boiling-point, which we indicate by S. This value is equal to 28·44° in the case of ether, that is, 1 mol. of any substance whatever dissolved in 99 mols. of ether raises the boiling-point of this liquid by 0·2844°. If g grams of a substance are dissolved in the weight corresponding with 1 mol. of the solvent (74 grams for ether), then, if the rise of the boiling-point is Δ, and the molecular elevation is S, we have : $S = \frac{\Delta}{g} m$, and from this we can deduce the molecular weight, m, of the unknown substance : $m = S\frac{g}{\Delta}$. Each solvent has its own characteristic constant, S, which may easily be determined, once for all, by employing a substance of known molecular weight.

Instead of being referred to the molecular weight of the solvent (ether = 74), these constants (for ether = 28·45) may conveniently be referred to 100 grams of the solvent (the value then diminishes, as the dilution is increased). Thus, for ether, S becomes 21·2, since : 28·44 : 100 = 21·2 : 74. On calculating the value of S in the same manner for various other solvents we find for : aniline, 32·2; phenol, 30·4; water, 5·2; benzene, 26·7; alcohol, 11·5; chloroform, 36·6; acetic acid, 25·3; carbon disulphide, 23·7; ethylene bromide, 63·2; nitrobenzene, 50; ethyl acetate, 25·1; acetone, 16·7; cyclohexane, 27·5 (Mascarelli, 1908).

If $\frac{g}{\Delta}$ is the specific rise per G grams of solvent, we find that per 1 gram of solvent the rise will be $\frac{g}{\Delta G}$, and for 100 grams of solvent, it will be $\frac{g \cdot 100}{\Delta G}$, and we thus arrive at the general formula, $M = S\frac{g \cdot 100}{\Delta G}$, in which all the magnitudes are known and determinable. In 1889 Arrhenius found from thermodynamical considerations that a relation exists between this constant, S, the latent heat of evaporation of the solvent, and its absolute boiling-point.

In 1889 Beckmann devised a very practical apparatus for the determination of molecular weights according to the above formulæ.

For dilute solutions there are differences of only 1° or 2° between the boiling-points of the solvent and solution, and very exact thermometers are thus necessary. As constructed to-day these are divided into fiftieths or hundredths of a degree, sometimes even into thousandths, with a scale 40 to 50 cms. long and a range of only 4° or 5°. Since the same solvents are not used for all substances, Beckmann ingeniously modified the upper extremity of the capillary tube containing the mercury, in a manner indicated in Fig. 27 (natural size), so that it was not necessary to construct such costly thermometers for each particular solvent, or to construct scales of immense length. In this way it is possible to measure the absolute difference of the boiling-point of the solvent and the solution with the same thermometer, whatever may be the solvent employed.

The scale of the thermometer indicates the relative boiling-points, that is, it indicates the points which the mercury column reaches when the solvent and the solution respectively boil. This may be explained more clearly by means of two examples.

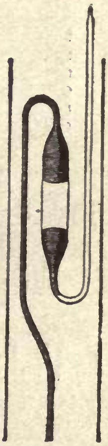


FIG. 27.

1. If a thermometer has been used beforehand for a lower temperature and is then required for a solvent boiling at a higher temperature, it is immersed in a bath which is 3° or 4° hotter than the boiling-point of the new solvent. By this means the excess of mercury rises in the capillary tube and into the small upper reservoir of the thermometer, forming a suspended droplet. If at this point a sudden shock is given to the thermometer, the droplet of mercury falls from the capillary column to the bottom of the little reservoir. On now removing the thermometer from the bath, the capillary mercury column descends into the lower bulb of the thermometer. The relative boiling-point of the solvent will then be indicated on the lower part of the scale, and that of the solution at a somewhat higher point.

2. In order to adjust the thermometer for a solvent which boils at a lower temperature, the instrument is inverted and subjected to a sudden shock, so that the drop of mercury contained in the small reservoir falls back on to the mouth of the capillary tube and adheres to this. At this point the thermometer is turned right way up and heated until the mercury in the bulb rises into the capillary tube and unites with the upper droplet; it is then immediately immersed in a bath 3° or 4° lower in temperature than the boiling-point of the new solvent. The excess of mercury at the upper extremity of the capillary column is made to fall by means of a sudden shock and the determination proceeded with as in the preceding example.

Since the same Beckmann thermometer is used for solvents which boil at very divergent temperatures, it is clear that the same quantity of mercury distributed in the capillary column indicates a different number of divisions when working at different temperatures. Hence, in very exact experiments, the readings of these thermometers must always be corrected by means of special tables which refer to particular temperatures.

To determine the molecular weight of a substance, we first read on the scale the division which the capillary column of the mercury reaches when the thermometer is immersed in a given weight of the pure boiling solvent (for example, 1·57°). A given weight of the substance under examination is then dropped into the solvent and the point is noted which the capillary mercury column reaches when the solution boils (for example, 2·09°). The absolute rise of boiling-point which results is then 0·52° (that is, 2·09° — 1·57°), and this suffices for the calculation of the molecular weight, as we already know the weight of the solvent and the weight of the dissolved substance.

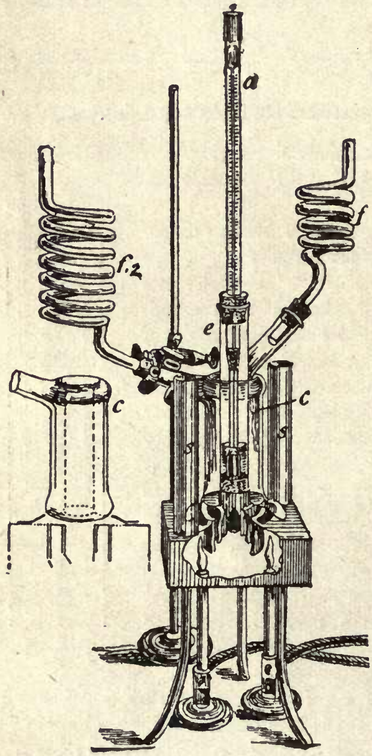


Fig. 28.

The complete apparatus is shown in Fig. 28. In order that the heat may be uniformly transmitted and the liquid may not be superheated, the vessel, *e*,—which has the form of a large test-tube with a side-tube connected with a cooling coil to condense the vapour of the solvent—has fused into its base either a piece of platinum wire surmounted with a polished garnet or glass bead, or a small piece of platinum foil. The test-tube is surrounded by a glass or porcelain cylinder with double walls, *c*, in which 20 to 30 c.c. of the solvent are vigorously boiled so as to maintain this mantle at a constant temperature. The side-tube of the mantle is also connected with a condensing coil or small condensing tube in order to condense the vapours. The thermometer dips into the solvent and almost touches the garnet.

This apparatus was again slightly modified by Beckmann in 1902 by causing the solvent to boil by means of internal circulation of the vapours of the external liquid. Later, in 1908, he also applied electrical heating, but the apparatus described above is still the one most commonly used.

The weighed substance, of which the molecular weight is to be determined, is introduced into the test-tube containing the weighed solvent—of which the boiling-point has already been determined with the thermometer—by means of a capillary U-pipette if the substance is a liquid, or in a glass capsule if it is viscous or solid, the coil, *f*, being momentarily removed.

In the case of solid substances, small pastilles may also be formed by means of a steel mortar and are then easily weighed.

The apparatus rests on a solid asbestos plate provided with two small asbestos chimneys for the escape of the burner gases. 40 to 50 grms. of solvent and about 0·2 grm. of the substance are ordinarily employed. When the first determination is finished, a fresh quantity of the substance is added to the same solution and the new boiling-point determined. A third and fourth addition may also be made so that several results are obtained and a more exact average thus deduced.

DETERMINATION OF THE FREEZING-POINT OF SOLUTIONS AND OF MOLECULAR WEIGHTS (CRYOSCOPY). As early as 1788 Blagden observed that the freezing-points of various aqueous solutions of the same substance are all more or less lowered as the quantity of dissolved substance is increased. This law was forgotten for many years, and in 1861 Rüdorff announced it as a new discovery, whilst in 1871 De Coppet, rediscovering the work of Blagden, pointed out its great importance.

It had been known since ancient times that the ice which separates from sea water is almost free from salt. This phenomenon was more carefully studied by Kries in 1814, and was discussed by Dufour, Rüdorff, and Fritsche about the year 1860. Many exceptions to Blagden's law are explained by the knowledge that various substances combine with the solvents. In 1871–1872 De Coppet determined the lowering of the freezing-point of various dissolved substances and water in relation to their molecular weights, and found that the molecular decrease of the freezing-point was almost constant for many different solutions (with the exception of ammonium nitrate, which dissociates in dilute solutions, etc.).

In 1882 Raoult extended these researches to many organic substances, dissolved both in water and in the purest benzene or acetic acid, and obtained for all of them molecular freezing-points which were equal and constant. With certain other solvents, he obtained doubled molecular weights. These exceptions were. however, explained later. When any substance which does not dissociate is dissolved in quantity in grams equal to the molecular weight in a litre of water, a lowering of the freezing-point of 1·85° is always found.

In 1885 Raoult proposed a very convenient method of determining the molecular weights of substances, based on his work on the lowering of the freezing-points of solutions. In 1886 Paternò and Nasini confirmed the value and practicability of the method proposed by Raoult, but the attention of chemists was only turned to it after the year 1890, when van't Hoff expounded, theoretically and mathematically, his brilliant theory of solutions (*see below*).

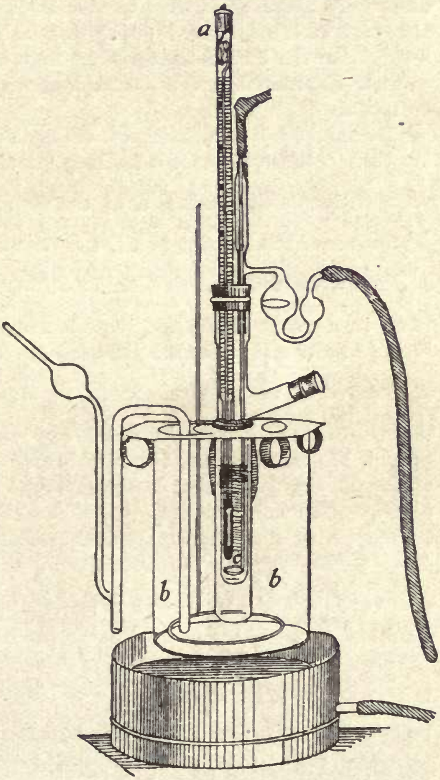


FIG. 29.

Various forms of apparatus are made for the practical application of this method, but the most convenient and the most used is that proposed by Beckmann in 1888.

The apparatus is constructed of glass and consists (as indicated in Fig. 29) of a large test-tube of 2½ to 3½ cms. diameter, with a side-tube for the introduction of the substance. The stopper with which it is closed carries a thermometer graduated in hundredths of a degree and a special tube through which passes a glass or platinum stirrer communicating with a bulb-tube containing concentrated sulphuric acid in order to prevent the entrance of moisture.

This test-tube is surrounded by another large tube so that the heat may be transmitted regularly. The whole is immersed in a large beaker which contains a freezing mixture to induce freezing of the solution.

An exact quantity (20 to 25 grms.) of solvent is placed in the test-tube so as to cover completely the bulb of the thermometer, the apparatus being arranged as is indicated in the figure and the solvent stirred continually until it freezes.

When the ice commences to separate from the solvent (the solid substance which separates will be termed *ice*, whatever the solvent may be) the mercury in the thermometer, which has been descending and oscillating, suddenly rises to the freezing-point and remains steady for some minutes. The highest temperature which is observed in two or three melting and freezing operations, carried out consecutively, is the true freezing-point of the solvent. When the ice is again melted a small quantity (0·1 to 0·2 grm.) of the substance under examination is introduced. Cooling is repeated until the ice separates and the freezing-point is noted. The ice is allowed to melt and again frozen, the temperature being noted each time, and the mean taken. After the ice has thawed, a further quantity of the substance is added and the new freezing-point of this more concentrated solution observed. Third and fourth quantities of the substance may then be introduced, so that about 1 grm. of substance is finally present in solution. The mean of the molecular weights found from the four determinations may be taken as the closest approximation, so long as these determinations are concordant with one another. Otherwise the mean must not be taken.

The method of calculating the molecular weight is analogous to that already employed for the ebullioscopic method. If g grams of a substance dissolved in 100 grams of solvent produce a depression, d, of the freezing-point of the solvent, then $\frac{d}{g}$ is the specific depression of the freezing-point, and on referring this to the molecular weight, m, of the substance, we obtain the molecular depression: $\frac{dm}{g}$. In this case also, acids and strong bases in aqueous solutions give abnormal molecular depressions of the freezing-point, because these substances are dissociated. The molecular weight, m, of any substance may be deduced by the following formula: $m = \frac{K}{A}$, where K is a constant depending only on the nature of the solvent (for water, 18·5; acetic acid, 39; formic acid, 27·7; benzene, 49; phenol, 74; naphthalene, 71; nitrobenzene, 70·7), and A indicates the specific depression of the freezing-point, that is, the quotient of the depression observed by the percentage content of the solution.

If g grams of substance are dissolved in G grams of solvent, they produce a lowering, Δ, of the freezing-point of the solvent; then, if the percentage content of the solution is x, $x = \frac{100g}{G}$, and the specific depression, A, will be: $A = \frac{\Delta}{\frac{100g}{G}} = \frac{\Delta G}{100g}$; knowing that $m = \frac{K}{A}$, we have: $m = \frac{K \,.\, 100g}{\Delta G}$. All these magnitudes being known or easily determined, the molecular weight can be calculated, and if with various solvents the same substance leads to various multiples, it is necessary to select the smallest value as the most correct molecular weight.

Example. Determination of the molecular weight of naphthalene ($C_{10}H_8$) by employing benzene as the solvent; 0·5507 grm. of naphthalene in 18·65 grms. of benzene produced a lowering of the freezing-point of 1·170°; the constant, K, for benzene is 59, and thus the molecular weight $m = \frac{49 \times 100 \times 0{\cdot}5507}{1{\cdot}170 \times 18{\cdot}65} = 124$, a value very near to the theoretical value, which is 128.

ANOMALIES IN CRYOSCOPY AND EBULLIOSCOPY. It has been observed that the molecular weights obtained by these two methods increase slightly as the solution becomes more concentrated, but the differences do not influence the results very much, because the method yields only approximate and not exact values for the molecular weights. In practice it is usually a question of deciding whether the substance under examination has a given molecular weight or one double or half as large.

The chemical nature of the solvent in relation to that of the substance has, on the other hand, a considerable influence on the results obtained.

These anomalies are due not to the dissociating action (into free ions) of certain solvents, such as water, alcohol, etc., of which we shall speak later (p. 94), but to the associating or polymerising action of certain solvents on the dissolved substance; the depression of the freezing-point or vapour pressure is thus smaller than it should be and the calculated molecular weights larger (up to two or three times) than the real values. This associating action is considerable when hydrocarbons (benzene, etc.) are used as solvents for substances containing hydroxyl groups (such as acids, alcohols, phenols, oximes, etc.), and the association or polymerisation increases rapidly with increase of the concentration where cryoscopic and ebullioscopic methods are applied.

The abnormalities are avoided in these cases by using as solvents substances containing hydroxyl groups themselves, for instance, acetic acid, as these have a depolymerising action.

Abnormalities also occur when the dissolved substance (solute) separates together with the "ice" of the solvent, or when vapours of the dissolved substance form together with those of the solvent. This occurs in the freezing-point method when the solvent is of analogous chemical composition to the dissolved substance, for example, if bromoform ($CHBr_3$) is used as a solvent for chloroform ($CHCl_3$) or iodoform (CHI_3), because then, as was pointed out by van't Hoff, mixed crystals separate (*see* p. 116); analogous ebullioscopic anomalies occur when the dissolved substance has also a certain vapour pressure, so that the vapour of the solute is found mixed with that of the solvent. In the first case abnormality is avoided by choosing as the cryoscopic solvent a liquid of different chemical character from that of the dissolved substance, and in the second case by using as the ebullioscopic solvent a liquid having a boiling-point much lower than that of the dissolved substance.

Hantzsch and also Oddo (1908–1909) recently studied the behaviour of various substances when pure concentrated sulphuric acid, free from sulphur trioxide and from water, is used as a solvent. They found that some substances, especially inorganic substances (potassium, sodium or ammonium bisulphate, etc.), which do not actually react with sulphuric acid, behave as electrolytes, because, according to the oxonium or hydronium hypothesis of Hantzsch, the substance and water itself unite loosely with sulphuric acid to give complexes dissociating into the corresponding ions: $HSO_4H + H_2O = HSO_4'(H_3O)^{\cdot}$, hydronium sulphate; $HSO_4H + NH_3 = HSO_4'(NH_4)^{\cdot}$, ammonium sulphate; $HSO_4H + O(C_2H_5)_2$ (ethyl ether) $= HSO_4'(HO(C_2H_5)_2)^{\cdot}$, diethyl hydronium sulphate, etc. The formation of these compounds was confirmed by F. Bergius (1910) by studying the electrical conductivities of the solutions.

RELATIONS BETWEEN RISE OF THE BOILING-POINT, DEPRESSION OF THE FREEZING-POINT, AND OSMOTIC PRESSURE OF DILUTE SOLUTIONS

In a very important treatise which has greatly helped the progress of chemical theory and practice during the last few years, and also obtained for him the first Nobel prize of £8000, assigned to him at the end of 1902, van't Hoff showed thermodynamically that certain relations exist between gaseous or vapour pressure, osmotic pressure, depression of the freezing-point and rise of the boiling-point of solutions.

The scientific and industrial bearing of this work has already been manifested by various very important applications.

We have seen how Avogadro's law for gases recurs in all the new methods of molecular weight determination with the sole difference that osmotic pressure is substituted for gaseous pressure.

We have shown how the fundamental formula for these methods may be derived from the general gas formula ($pv = RT$) with the help of the constant R; we deduced this constant (R) from the osmotic pressure of a sugar solution (p. 83).

With the help of a hypothetical experiment due to Arrhenius in 1889, we are able to show from first principles the relation between osmotic pressure and the diminution in the vapour pressure of solutions. We introduce a given solution, L, into a vessel shaped like an inverted thistle-funnel with a long neck and closed at the base by a semi-permeable membrane (Fig. 30). We then immerse the wide portion of this instrument in a vessel containing the pure solvent, *F*. The whole is covered by a tall bell-jar, which is evacuated. Osmotic action occurs between the solution, *L*, and the solvent, *F*, and the solution will rise in the tube of the funnel to a certain height, *h*. Equilibrium will be established when the pressure exerted by the column of liquid, *Gh*, is equal to the osmotic pressure of the solution.

In the interior of the bell-jar liquid evaporates both from the surface of the solvent, *G*, and from the surface, *h*, of the solution, and it is quite clear that the vapour evolved at *h* supports the pressure of all the vapour which is formed below, and that the vapour formed in *G* must equalise the pressure of the vapour formed above; thus the vapour of the solvent at the height *h* supports the same weight as the vapour of the solution at height *h*, that is, it has the same vapour pressure.[1] If one supposes that there are *n* molecules of the dissolved substance and *N* molecules of solvent in the solution, the osmotic pressure of the solution may be represented by the general gas formula, because we have seen that the dissolved substance will cause the same pressure, *p*, as it would cause if present in an equal volume as gas (*see* p. 83).

Hence $pv = nRT$, that is, $p = \frac{nRT}{v}$, *R* being 84,700 and *T* indicating the absolute temperature. In order to find the value of *v* we must remember that *N* molecules of the solvent have a weight *MN*, where *M* is the molecular weight, and if *S* indicates the specific gravity of the solvent, then $v = \frac{MN}{S}$. Introducing this value of *v* into the general formula, we obtain: $p = \frac{nRTS}{MN}$, if we suppose that the pure solvent and the very dilute solution have the same volume.

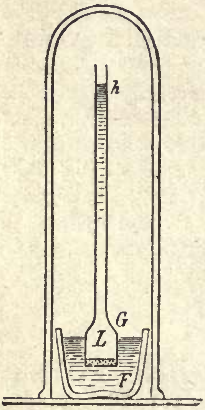


Fig. 30.

The difference between the vapour pressure of the solution (f') and that of the solvent (f) is, however, equal to a column of vapour of the height *h* and of 1 sq. cm. cross-section (if we express the pressure in grams per sq. cm.), and the density of the vapour being *d*, we have: $f' = f - hd$. This value may also be obtained from the general formula given above by substituting the corresponding values, and we then arrive by suitable manipulation at the same formula as that of Raoult, namely, $\frac{f-f'}{f} = \frac{n}{N}$, where we have *N* instead of $N + n$, because we are considering a very dilute solution in which the value of *n* is so small that it may be neglected in comparison with *N*. The close relation between the osmotic pressure and the vapour pressure is now evident, as is, therefore, also the relation between the corresponding methods of determining molecular weights.

It is now easy to show that the method of molecular weight determination by means of the lowering of the freezing-point of solutions is founded on the same principle as that of the diminution of the vapour pressure.

The relation between the vapour pressure of the frozen solvent which

---

[1] No other supposition is possible. If, indeed, the vapour at the height *h* had a lesser vapour pressure than the solution in *h*, then liquid would distil from the solution and these vapours would join those of the solvent to establish equilibrium; this distillation would also increase the concentration of the solution in *h* and consequently the osmotic pressure, so that fresh solvent would penetrate into *L* through the membrane, and the new liquid would again be evaporated in *h* so that we should have a case of perpetual motion in contradiction to the second law of thermodynamics. If we take the reverse hypothesis, which is that the vapour of the solvent at the same height, *h*, has a larger vapour pressure than that of the solution at the same height, then the vapour of the solvent would necessarily condense at the surface of the solution, which would become diluted until its vapour was in equilibrium with that of the solvent in *h*; this dilution would, however, diminish the osmotic pressure of the solution, causing a part of the liquid to issue through the membrane at the base, and we again arrive at the absurdity of a perpetual motion, because condensation of the vapours in *h* would recommence. Thus the only possible hypothesis is that which supposes the solvent and the solution at the height *h* to have the same vapour pressure. Then we have equilibrium and the phenomenon can be clearly explained.

separates from a solution and the vapour pressure of the solution itself was stated empirically and proved experimentally by Raoult in 1878, but Guldberg deduced it mathematically in 1870.

We will imagine a curved glass tube closed to form a ring (Fig. 31) and containing a dilute solution, *b*, of a solid substance in a liquid; the tube above the solution has been evacuated and is thus filled only with the vapour of the solvent. If we now cool the tube so that a little of the frozen solvent separates in *a* and floats on the solution, the vapour pressure of the solution and that of the frozen solvent at the temperature at which it commences to separate must necessarily be equal. If the vapour pressure of the frozen solvent in *a* were greater than that of the solution in *b*, part of the frozen solvent would distil over and condense in *b*, thus diluting the solution, but since on dilution the freezing-point is raised, new frozen solvent will separate in *a* and consequently a further portion of frozen solvent will distil as at first, so that we arrive at the absurdity of perpetual motion.

If we imagine the reverse case, that is, that the vapour pressure of the solution is greater than that of the frozen solvent in *a*, then the solvent will distil from *b* and be condensed as frozen solvent in *a*; the solution in *b* will then become more concentrated and its freezing-point will be lowered. Consequently a part of the frozen solvent in *a* will dissolve and a new portion will be formed by condensation of the vapours of the solvent, so that perpetual motion will again occur.

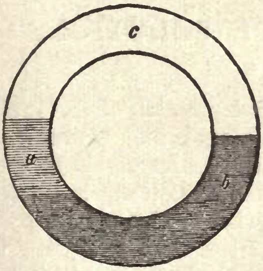


FIG. 31.

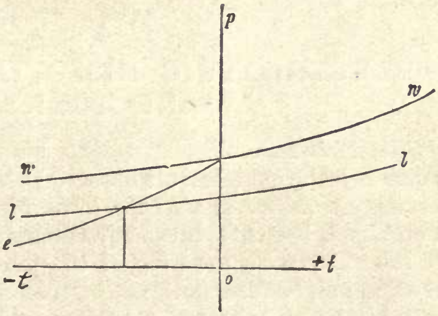


FIG. 32.

A plausible explanation of the phenomenon can thus be attained only by supposing that at the temperature of freezing, the vapour pressures of the frozen solvent and of the solution are equal, so that the equivalence of the cryoscopic and ebullioscopic methods of determining the molecular weights is proved.

We may also prove this fact by a graphic method in the following manner. We imagine a system of co-ordinates in which the abscissæ indicate the temperatures $-t$ to $+t$, and the ordinates the vapour pressures (Fig. 32).

The curve *n* indicates the vapour pressures of water at various temperatures (even when the liquid is kept below 0°); *e* is the vapour pressure curve for ice, meeting that for water at a certain angle at 0° (Kirchhoff). If *l* is the vapour pressure curve of a given solution at a different temperature, then the point where *e* meets *l* indicates the temperature at which experimentally the solution commences to separate ice, but also indicates that at this point the vapour pressures of the solution and of the ice are equal.

The connection between osmotic pressure, vapour pressure, lowering of the freezing-point and rise of the boiling-point of dilute solutions is thus evident.

DEDUCTION OF THE MOLECULAR WEIGHT FROM THE ACTION OF TWO SOLVENTS ON THE SAME SUBSTANCE

In 1872 Berthelot and Jungfleisch observed regularities in the method of distribution of a substance between two superposed solvents which do not mix. If one of the solvents, *A*, is slightly soluble in the other, *B*, the solubility being *l*, then the vapour pressure of the latter will diminish and will correspond with a certain osmotic pressure. If n molecules of another substance are dissolved in N molecules of A, the solubility of A in B will diminish and will now be equal to l', and we then arrive at a formula analogous to that already obtained for the determination of molecular weight by means of the vapour pressure: $\frac{l-l'}{l'} = \frac{n}{N}$. If we express n by the weight, p, of the substance divided by the unknown molecular weight $\left(n = \frac{p}{m}\right)$, and replace N by known magnitudes, namely, the weight P and the molecular weight, M, that is, $N = \frac{M}{P}$, we have all the data necessary to calculate the molecular weight.

In 1889–1890, Nernst actually dissolved a liquid, A, in another liquid, B, until this was saturated and then froze the solution. In the solid solvent which separated, A and B were found (not the solvent B alone, because the solution was saturated). He then added a substance soluble in A, and since the solubility of A in B was thus diminished, the freezing-point was raised by a quantity which bore a certain ratio to the amount of dissolved substance.

This method is not much used, but in certain cases has given very exact results.

ELECTROLYTIC DISSOCIATION OF SOLUTIONS AND IONIC THEORY

In determining molecular weights by means of the depression of the vapour pressure of solutions, Raoult observed that on dissolving 1 mol. of numerous substances in a litre of water, a lowering of the freezing-point of about 1·85° was obtained, but that dilute aqueous solutions of acids and strong bases or of their salts showed a lowering of the freezing-point, rise of the boiling-point, and osmotic pressure noticeably greater than those corresponding with the true molecular weights. For dilute solutions of hydrochloric acid the displacements of the boiling- and freezing-points were approximately doubled; for sulphuric acid they were trebled, etc. Thus, per litre of water, only about 18·3 grms. of hydrochloric acid were needed instead of 36·6 grms. in order to depress the freezing-point by 1·85°.

Solutions giving these abnormal values also behave in an abnormal manner with regard to the refraction of light, magnetic rotation, optical rotation, etc.

In 1887 the Swedish physicist, Svante Arrhenius and, simultaneously, Planck, explained all these apparent abnormalities by means of a simple and equally brilliant hypothesis which then became the indispensable foundation for explaining all electrolytic phenomena.

Arrhenius was, in fact, able to demonstrate that all these numerous exceptions were shown by solutions which conducted the electric current, that is, by electrolytes, to which various aqueous solutions of acids, bases, and salts belong. Water itself is not an electrolyte, but if an acid, a base, or a salt is added to water it then allows the electric current to pass and this causes the separation at the respective poles of the components of the dissolved substance. In order to explain all these facts, Arrhenius supposed that the molecules of such substances, on entering into solution, were dissociated into two or more parts which he called *ions*, a name already used by Faraday. These ions carry a high electric charge (96,540 coulombs, or a multiple of this quantity for each monovalent gram-ion). The name *anions* is given to those which carry a negative electric charge and move in a direction contrary to the electric current and thus collect at the *anode* (positive pole), where they give up their electric charge and separate in the atomic or molecular condition; *cations*, on the other hand, carry an electro-positive charge, move in the same direction as the current (from the positive to the negative pole), and separate at the *cathode* (negative pole).

Substances giving aqueous solutions which exhibit abnormal osmotic pressures or depressions of the vapour pressure or freezing-point and which conduct the current, when dissolved in certain other substances no longer conduct the electric current, and then show normal osmotic pressure and normal depression of the vapour pressure and freezing-point.

It is evident then that electrical conductivity is closely connected with the dissociation of the molecules into ions, that with certain solvents this electrical dissociation (so easily obtained with water) does not occur, and that the current does not then pass. A minimal or partial dissociation of the molecules into ions suffices, however, to cause electrical conductivity, the extent of which increases with the ionic dissociation.[1]

In dissociated, dissolved *salts*, the *cation* is usually formed of a metal and the *anion* of an acid residue. All dissolved and dissociated *acids* are, on the other hand, characterised by the hydrogen *cation* H, whatever may be the rest of the molecule forming the anion. All dissolved and dissociated *bases* are characterised by the *anion* OH, which is common to all of them, whatever may be the cation forming the rest of the molecule.

The characteristic ions of acids (H) and of bases (OH) have the property of modifying the colour of *indicators* (*see below*) and of causing certain catalytic reactions (*see below*).

All hydrogenated substances are not acids, but all are acids which dissociate to a greater or less extent in aqueous solution with production of hydrogen ions.

The hydrogen characteristic of any acid substance is freely evolved when this is mixed with powdered magnesium, and often even with other metals,

---

[1] We find in nature substances which conduct, and others which do not conduct electricity. Electric conductors may be divided into three classes. Conductors of the first class are those which conduct the electric current and are at the same time heated without being altered chemically and without transportation of matter. Metals belong to this group, and their conductivity increases with fall of temperature. Conductors of the second class are aqueous solutions of salts, acids, or bases, which allow the electric current to pass, but with simultaneous decomposition of the molecules of the dissolved substance into the corresponding ions, which are carried to the poles of contrary sign. The electrical conductivity of such conductors increases with elevation of the temperature. Conductors of the third class are the gases, especially at reduced pressure, and their conductivity diminishes with increase of the pressure. Gases at the ordinary pressure are not generally conductors of electricity, but they become so under the influence of certain ultra-violet radiations or cathodic or radio-active emanations. Gases with monatomic molecules (argon, helium, neon, etc.) are the best gaseous conductors of electricity.

Aqueous solutions of organic compounds other than acids, bases, and typical salts, are not electrolytes. No organic or inorganic substance is an electrolyte when dissolved in benzene, carbon disulphide, ether, or similar solvent. Sugar does not conduct the electric current even when dissolved in water. In aqueous solution neutral salts are the most highly dissociated; at moderate concentration half their molecules are dissociated; in dilute solution the dissociation is almost complete. There are also other solvents than water, such as alcohol, hydrocyanic acid, etc., which in certain cases give dissociated solutions, these being good conductors of the electric current.

Water is the best medium for producing ionic dissociation on account of its high dielectric constant. The *dielectric constant* is the ratio between the charges which can be maintained between the two armatures of an electric condenser when water and air respectively are interposed between them. If the charge which can be maintained in air is taken as unity, that maintained in presence of water = 81, which is the dielectric constant of water. The constant varies with the nature of the dielectric (or insulator). It is relatively small for certain organic solvents, such as ether, carbon disulphide, etc., which, in fact, form solutions of electrolytes exhibiting very little dissociation; on the contrary, there are substances other than water, even some of minimal electrical conductivity but with a high dielectric constant, such as liquid sulphur dioxide, hydrocyanic acid, and liquid ammonia, which have considerable dissociating power. Pure liquefied hydrogen chloride has a very small dielectric constant, and this explains why, although it dissolves certain salts readily, the solutions obtained are not good conductors of the electric current, because no ionic dissociation is produced. Alcohol, on the other hand, has a fairly high dielectric constant, and consequently a dissociating or ionising power which is about one-quarter that of water.

such as zinc, iron, etc. In order that electrolytic dissociation may occur, a solvent is required, which is ordinarily water.

Further, acids have a special taste, redden blue litmus solution, form salts by combining with basic substances or with metals (in the latter case hydrogen is developed) and also possess certain catalytic properties which we shall study in connection with organic chemistry, *e. g.*, the inversion of sugar, hydrolysis of maltose, etc.; all these properties are manifested when dissociation of the molecules occurs, that is, when the hydrogen is present in the form of a cation, so that the acid reaction is ordinarily observed in presence of water or moisture.

Even the most energetic acids, when absolutely deprived of water, no longer give any of the characteristic actions which we have enumerated. Thus, pure anhydrous hydrochloric acid, whether gaseous or liquefied, does not react with metals and no longer reddens dry blue litmus paper, whilst in the dilute condition it reacts energetically. Large quantities of the more energetic acids, such as sulphuric acid, are to-day transported with the greatest security in iron tanks, mounted on railway cars, because it is quite easy to obtain such acid free, or almost free, from water, and there is then no danger of the iron being corroded, since the molecules of sulphuric acid are not dissociated and the chemical reactions are produced only by the ions.

The characteristic properties of dissolved acids can be completely modified or neutralised by means of the action of basic substances. These bases are usually substances which turn litmus solution, which has been reddened by acids, blue. They have a special taste, cause various catalytic reactions of organic compounds, saponify fats and esters, etc. Most of the bases are obtained by dissolving oxides of metals in water, and in aqueous solution they form free characteristic ions consisting of the OH (hydroxyl) group. Potassium hydroxide, KOH, for example, is dissociated into the cation K and the anion OH. If to the solution of an acid which has been reddened by litmus we add a solution of a base, drop by drop, the H cations of the acid gradually unite with the OH anions of the base to form undissociated water, and we thus arrive finally at a point at which all the cations of the acid are transformed into water; the solution then has a neutral reaction. A single drop of the base in excess immediately changes the colour of the solution to blue, because free OH anions of the base are then present. In the case, for example, of solutions of HCl and of KOH, when the mixture is neutral, that is, when all the acid cations and basic anions have disappeared, Cl anions from the acid and K cations from the base will remain in solution as the ions of the salt (potassium chloride, KCl), which is thus formed by the exact neutralisation of the acid by the base. In general, salt formation always occurs when the characteristic hydrogen of an acid is replaced by a metal.

When we have a salt in dilute aqueous solution, we find it to be dissociated into the corresponding ions; for example, sodium chloride (NaCl) is dissociated into chlorine (Cl) anions and sodium (Na) cations. At first sight it may appear strange that sodium, which reacts so energetically with water and decomposes it at once when brought into contact with it, should exist in the free condition in aqueous solution without reacting, and also that chlorine, which we know as a greenish-yellow gas of suffocating odour, should exist free as an ion without making its presence known. This is, however, because we are accustomed to characterise these substances, Na and Cl, in the free atomic or molecular state, but not in the state of dissociation as ions with an electric charge of 96,540 coulombs per gram-ion, and thus kept in equilibrium with one another by means of equal charges of contrary sign. The properties of the ions are very different from those of the molecules, especially as regards the nature and quantity of the energy contained in them.

These properties of solutions are therefore those, not of the dissolved salts themselves, but of the free ions of the salts.

DOUBLE DECOMPOSITION OF SALTS. By means of the hypothesis of the electrolytic dissociation of salts in solutions, the so-called double decomposition of salts is explained. It was at one time believed (by Berthollet in 1803 and by Guldberg and Waage later) that on mixing the solutions of two salts the resultant solution would contain four salts formed by partial reciprocal decomposition—supposing that no precipitation occurred. It was also believed that the quantities of the four salts varied according to the preponderance of one or other of the two salts primarily mixed, and thus on mixing, for instance, solutions of equimolecular quantities of NaCl and KI, it was believed that in the new solution portions of NaI and KCl were also present; this was considered to be proved by the fact that on gradual evaporation of the solution of the mixture, the new salts actually separated. When coloured salts were mixed, change of colour of one or the other was also observed; thus, on mixing $CuSO_4$ with NaCl, the solution acquired a greenish tint, which was attributed to the formation of $CuCl_2$. When, however, the solubility relations in the solution are not altered, the formation of new salts should be accompanied by the development or absorption of heat (increase or diminution of energy). In normal cases, however, no thermochemical alteration was observed, the formation of new chemical compounds, that is, of new salts, being thus excluded.

By means of the ionic theory this phenomenon can be completely explained. In the case, for instance, of two dilute solutions of NaCl and KI, these salts must be considered as mainly dissociated into the respective ions Na, Cl, K, and I, but the same is the case in a solution of KCl and NaI, obtained directly from the two salts or by the mixture of their respective solutions, so that the same ions are always present, and therefore Na, K, Cl, and I are present without any chemical reaction occurring.

On the other hand, since the various characteristic chemical reactions of individual salts in solution are due to the free ions and not to undissociated molecules of the salts, we shall have the same characteristic reactions in an equimolecular solution of NaCl and KI, as in an equimolecular solution of $KCl + NaI$ or any mixture of these two solutions. If, therefore, the equilibrium between these ions is altered by the separation of part of the ions in the form of insoluble or less soluble salts, a reaction will really occur, so that, in the ordinary way, the reaction proceeds entirely in a given sense. Thus, when the solution is concentrated by evaporation, at a certain point those ions will unite and separate which form a less soluble salt (*see* preparation of potassium nitrate or conversion nitrate). Again, when barium chloride is added to a solution of sodium sulphate, barium sulphate is formed and separates, because it is insoluble, and all the sodium sulphate can be transformed and separated in the form of insoluble barium sulphate. These true chemical reactions are, however, accompanied by measurable thermal phenomena.

The same may be said when, by mixing two electrolytes, two of the four types of ions which are formed have great affinity for one another and unite to form a substance which has little tendency towards dissociation. In this case true combination of the ions, that is, true chemical combination, occurs. Thus, when two strongly dissociated substances, such as hydrochloric acid solution and sodium acetate, are mixed, the formation of NaCl and acetic acid is possible, but NaCl has a great tendency to dissociation and is therefore not formed, whilst, on the other hand, acetic acid is a weak acid, thus only slightly dissociated and the affinity between the H ions and those of the acetic acid is very great; undissociated acetic acid is, therefore, easily formed. This fact explains why in practice the strong acids readily liberate the weak acids from their salts, and why strong bases liberate weak bases from their salts; the H cations of the acid have a great affinity for, and tend to unite with, the anions of the weak acid, whilst the OH anions of the base have a great affinity for, and tend to unite with, the cations of the weak base. Thus, caustic soda liberates ammonia from ammonium salts.

In 1908 Rosenstiehl stated that double decomposition between salts, as in the case of organic esters, is always preceded by hydrolysis, by means of an intermediate reaction with one or more molecules of water, for example: $MCl + HOH = MOH + HCl$; $[+ AgNO_3] = AgCl + M \cdot NO_3 + H_2O$. He called salts and esters which are slowly hydrolised *bradolytes*, whilst those which are rapidly hydrolised he named *stenolytes*.

ANALYTICAL TESTS FOR THE IONS. The extraordinary simplicity of the tests used in analytical chemistry is explained by the ionic theory, because in a solution of many salts we do not require to recognise the properties of all the salts, but simply those of the respective ions, which possess properties common to many salts. If, for example, we have a solution which contains 50 anions and 50 cations, these would theoretically be able to form 2500 salts, and if all these salts possessed individual characteristic reactions, it would be necessary to verify the presence of 2500 substances. Since, on the other hand, salts in aqueous solution are dissociated into their ions, all that is necessary to analyse this solution completely is to confirm the presence of 100 ions (50 anions and 50 cations).

Further, apparent abnormalities in analytical chemistry can also be explained by the new theory of electrolytic dissociation. We know, for example, that silver nitrate is the most certain reagent, and is almost universally employed, for the detection of chlorine, because the cation of silver (in the soluble nitrate) unites with the anion, chlorine (of any soluble chloride) with the separation of the white insoluble substance, silver chloride. Now, whilst this reaction occurs with hundreds of chlorinated compounds and with all soluble chlorides, certain other compounds which also contain chlorine, such as potassium chlorate, chloroform, chloroacetic acid, etc., give no precipitate with silver nitrate.

By the electrolytic dissociation theory we know that the formation of silver chloride by means of soluble silver salts is a reaction characteristic of chlorine ions, whereas chloroform is not a salt and is not dissociated, and therefore cannot give this reaction. Potassium chlorate (ClO_3K) is a salt, but in aqueous solution it is dissociated into its ions, one of which is potassium (K) and the other the chloric acid residue (ClO_3), which is different from the chlorine ion and thus does not give the reaction with silver nitrate.

VALENCY OF THE IONS. Molecules dissociated into two ions also exert double the normal osmotic pressure, and in the case of very dilute sulphuric acid, three times the osmotic pressure which would be deduced from its formula is obtained. This is easily explained by the theory of electrolytic dissociation. The sulphuric acid molecule, H_2SO_4, is, in fact, dissociated into the divalent anion SO_4, and two monovalent cations (2H), that is, into three ions altogether, these exerting an osmotic pressure three times that which would be due to the undissociated molecule. The osmotic pressure is thus strictly dependent on the number of free ions and not on their nature. This valency of the ions corresponds exactly with the valency which has already been studied and deduced from atomistic considerations and from analytical or stoichiometrical results.

The valency of cations is indicated by dots to the right of the symbol at the top, whilst that of the anions is indicated similarly by dashes, and we thus have the cations $H^{\cdot}$, $K^{\cdot}$, $Ba^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, etc., and the anions Cl', S'', etc. Apart from the simple ions, others are known of complex composition, such as SO_4'', NO_3', etc. All monovalent ions have an equal electric charge of 96,540 coulombs. The valency of these ions may be deduced from the relation between the quantity of electricity with which the polyvalent ions are charged and the quantity carried by a monovalent ion. The divalent ions have a double electric charge, etc.

The electrolytic behaviour of sulphuric acid also explains why this acid is dibasic, that is, why it is able to saturate two basic monovalent radicals, or one divalent basic radical; thus, the basicity of an acid may also be deduced from the number of H cations corresponding with its anions.

In the dissociation of bases we always find the hydroxyl anion, OH, which is monovalent. Thus, for sodium hydroxide we have:

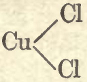
$$NaOH = \underset{+}{Na^{\cdot}} + \underset{-}{OH'};$$

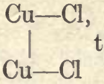
this base is hence monoacid, that is, the saturation of its anion requires a single cation of an acid. One molecule of a monoacid base will be saturated, then, by one molecule of a monobasic acid (for instance, hydrochloric acid, HCl). The molecule of barium hydroxide, on the other hand, forms three ions; $Ba(OH)_2 = \underset{+}{Ba^{\cdot\cdot}} + \underset{-}{OH'} + \underset{-}{OH'}$; thus this base is diacidic, that is, its divalent cation corresponds with two monovalent ions, and one molecule will be saturated by one molecule of a dibasic acid or by two molecules of a monobasic acid.

It is important to note that the charge of the same ion may vary in various salts. Thus the ferrous-ion in ferrous sulphate ($FeSO_4$) is divalent: $FeSO_4 = Fe^{\cdot\cdot} + SO_4''$, whilst in ferric chloride ($FeCl_3$), on the other hand, iron is trivalent:

$$FeCl_3 = \underset{+}{Fe^{\cdot\cdot\cdot}} + \underset{-}{Cl'} + \underset{-}{Cl'} + \underset{-}{Cl'}.$$

When the polyvalent cation of a metal combines with several chlorine ions (monovalent), the quantity of electricity corresponding with the metallic cation is a multiple of that corresponding with the monovalent chlorine-anion; that is to say, it is equal per gram-ion to as many times 96,540 coulombs as there are chlorine-ions corresponding with one ion of the metal, so that each valency corresponds with a definite quantity of electricity.

On electrolysing cupric chloride  a given quantity of electricity separates 31·8 grms. of copper for every 35·5 grms. of chlorine, or 63·6 grms. of copper (gram-ion) per 71 grms. of chlorine (gram-ions corresponding with two valencies).

On electrolysing cuprous chloride,  $\begin{array}{l}Cu—Cl,\\ |\\ Cu—Cl\end{array}$ the same quantity of electricity separates double the quantity of copper, that is, 63·6 grms. of copper for each 35·5 grms. of chlorine; thus in cupric chloride we have a simple divalent copper cation, $Cu^{\cdot\cdot}$, and 31·8 grms. of copper for every gram-ion of monovalent chlorine Cl', whilst in cuprous chloride we have a compound divalent cation of copper, $Cu_2^{\cdot\cdot}$ and 63·6 grms. of copper for each gram-ion of monovalent Cl'. For this reason in practice salts with a minimum valency are electrolysed whenever practicable, because for a given consumption of energy a greater quantity of metal is separated in this way.

We have thus arrived at conceptions of ionic valency without any addition to the atomic hypothesis, simply basing our considerations on the electrolytic behaviour of many substances in dilute solution, and we see how in these phenomena also we obtain a proof of the existence of variable valency, in distinction to the constant valency which, on exclusively atomistic conceptions, was assumed until a short time ago. We have also shown that valency is generally lower at high temperatures at which compounds in a state of minimum oxidisation are often found, whilst at lower temperatures the compounds are more stable and are generally present in a more highly oxidised condition.

MOLS, NORMAL SOLUTIONS, AND VOLUMETRIC ANALYSIS. The behaviour of acids and bases in solution serves as the basis of a whole section of analytical chemistry, that of volumetric analysis.

Bases and acids neutralise one another through the reciprocal saturation of their characteristic ions. A divalent ion is equivalent to two monovalent ions, and three of the latter are equivalent to one trivalent ion. The quantity of matter which corresponds with each valency of the ions is the same as that which we know under the name of combining weight or equivalent or stoichiometric value (*see* p. 21); thus, if a quantity of an acid or base corresponding with its equivalent expressed in grams, *i. e.*, its gram-equivalent (this is the quantity corresponding with one valency, or with a monovalent ion), is dissolved in one litre of aqueous solution, such a solution is called a *normal solution.* Such solutions are used for the determination of the strength or concentration of any acid or base, that is, for the determination of the quantities of pure acid or base contained in a given volume of their solutions, no matter how such volume may be diluted.

For the sake of brevity in the discussion of electrolytic phenomena, the use of the word *mol* to express the quantity in grams corresponding with the molecular weight of a substance has been proposed; it was then found more practicable to call the quantity in grams corresponding with the ion, a *mol-ion* (gram-ion); thus one mol-ion of $Cl = 35{\cdot}5$ grms.; one mol-ion of $H = 1{\cdot}01$ grms.; one mol-ion of $SO_4 = 96$ grms., etc.

Hence, in order to obtain a normal solution of hydrochloric acid (HCl), we must dissolve the quantity of HCl corresponding with one mol-ion of hydrogen (that is, to 1·01 grms., or 36·46 grms. of pure HCl) in sufficient water to form one litre of solution.

In order to obtain a normal solution of sulphuric acid, which contains a divalent SO_4'' anion corresponding with two monovalent $H^{\cdot}$ cations, we must dissolve the quantity corresponding with one mol-ion of H only, that is, $\frac{H_2SO_4}{2} = \frac{98}{2} = 49$ grms. of the pure acid, in sufficient water to form one litre. In this case equal volumes of the normal solutions of HCl and of H_2SO_4 are equivalent and will neutralise the same quantity of a basic substance.

The normal solutions of bases always refer to one gram-ion of OH, and in the case of polybasic bases, a quantity in grams is used corresponding with one OH anion, that is, with one mol-ion of OH. Equal volumes of normal solutions of an acid and of a base exactly neutralise one another, because the OH' anions of the base unite with the $H^{\cdot}$ cations of the acid to form undissociated water, which is neutral. The point of neutrality is rendered evident by the employment of indicators which indicate colorimetrically the acid or alkaline reaction of the acids or bases.[1]

---

[1] *Indicators* are weak organic acids or bases, and are therefore only very slightly dissociated. The non-dissociated portion has a varying colour corresponding with the free ions, and since the typical $H^{\cdot}$ and OH' ions are not coloured, the coloured portion of basic indicators will be the cation and the coloured portion of acid indicators the anion. Ordinarily acid indicators are used, and not salts, because these are more highly dissociated. When a strong acid is titrated with a base, employing an acid indicator, the numerous $H^{\cdot}$ cations of the strong acid completely suppress the dissociation of the indicator. As the base is gradually added during titration, the $H^{\cdot}$ cations of the strong acid gradually disappear, since they unite with the OH' anions of the base to form undissociated water. When, however, all the $H^{\cdot}$ cations are saturated, a single drop of the base in excess causes formation of salts of the indicator and these easily dissociate, giving the free anion, the characteristic colour of which indicates the end of the titration (neutralisation).

The titration is complete even when the substance being titrated is not highly dissociated, because even if an acid is not highly dissociated and only a part of its cations $H^{\cdot}$ are in the free state (actual ions), these are in a certain equilibrium with the remaining acid hydrogen which is not dissociated (potential ions), and as the basic solution employed in the titration gradually reacts, the actual ions are used up in the formation of water; the equilibrium between the actual and potential ions of the acid being thus disturbed, a part of the latter immediately dissociates, giving actual ions to restore the equilibrium. The titration process continues in this manner until all the $H^{\cdot}$ ions of the acid (including those which were not at first dissociated) have reacted with the hydroxyl of the base. Thus, during titration, in general *all the acid hydrogen reacts,* and not merely the hydrogen which is dissociated in the form of ions.

In order to measure the quantity of actual ions of an acid or a base, that is, to ascertain its degree of dissociation, it is necessary to measure the electrical conductivity of the solution.

If a very weak acid is to be titrated, its dissociation is small and the number of $H^{\cdot}$ cations is not sufficient to prevent slight dissociation of the indicator. In these cases, therefore, there is not a sharp change of colour when the neutral point is passed, and the titration remains uncertain and inexact. This difficulty is avoided by using very weak indicators, such as phenolphthalein or litmus, and by titrating with a strong base. Weak bases should be titrated with a strong acid and a strong indicator, such as methyl orange: when dissociated, this preserves its characteristic colour even at points very close to the neutral point, but as soon as this is passed to the extent of one drop of the strong acid, the $H^{\cdot}$ cations of the latter immediately and completely repress all dissociation of the indicator and its colour is changed. In general, the titration of weak acids with weak bases and *vice versa* should be avoided. When a strong acid is titrated with a strong base, any indicator whatever may be used, but if a salt with a weak cation, such as ammonium

By means of a normal solution of HCl we can always determine the quantity of sodium hydroxide contained in any solution, because we know that 36·46 grms. of HCl neutralise 17 grms. of the basic OH ion, or corresponding quantities of basic substances. In the case of sodium hydroxide, we have 23 grms. of sodium united to the anion OH, so that 36·46 grms. of HCl correspond with 40 grms. of NaOH $(23 + 17 = 40)$.

In the other case, with a normal solution of a base we are able to determine the concentration of any acid solution; 1 c.c. of normal NaOH solution corresponds with 0·03646 grm. of HCl, 0·049 grm. of H_2SO_4, etc.

The equivalence of the normal solutions which serve as standards in volumetric analysis is also easily explained by the fact that on neutralising equivalent quantities of strong bases with a given quantity of strong acid, the same quantity of heat is always developed; this is the *heat of neutralisation*, which is proportional to the number of ions which unite to form water, independently of the nature of the acid and the base.

$$NaOH' + H{\cdot}Cl' = Na{\cdot}Cl' + H_2O + 13700 \text{ cals. (due to } H^{\cdot} + OH' = H_2O)$$
$$K{\cdot}OH' + H{\cdot}NO_3' = K{\cdot}NO_3' + H_2O \ldots\ldots + 13700 \text{ cals.}$$

$Ca^{\cdot\cdot}(OH)_2' + 2H^{\cdot}Cl' = Ca^{\cdot\cdot}Cl_2' + 2H_2O \ldots + 27400$ cals., that is, double the amount of heat, because $2H^{\cdot}$ cations unite with $2OH'$ anions.

We may also consider the ions of non-dissociated molecules to be held together by large amounts of chemical energy, whilst those of the greatly dissociated substances have less affinity for one another, their independent existence in solution being thus explained. The dissociation of water is extraordinarily small (its dissociation constant being estimated at about 10^{-14} at ordinary temperatures, whilst at 50° it is three times larger), because the $H^{\cdot}$ and OH' ions have a strong mutual affinity and always tend to combine to form undissociated water. We can thus easily explain why, when equal volumes of equivalent solutions of acids and bases are mixed, all the $H^{\cdot}$ and OH' ions unite to form neutral water until a new equilibrium is established in correspondence with the minimal dissociation of water (10^{-14}). Therefore, whatever may be the acids and bases which react, the heat developed is always that due to the total transformation of the $H^{\cdot}$ and OH' ions into H_2O. When, on the other hand, dilute salt solutions are mixed, there is no evolution of heat, because the ions are free both before and after mixing and no combination occurs, though the contrary was believed at one time.

HEAT OF FORMATION OF THE IONS. After the above considerations we are able to deduce also the heat of formation of the ions. The heat evolved in reactions between acids and bases, as shown by the above equations, is due simply to the formation of water by the union of $H^{\cdot}$ and OH' ions.

It is evident that whatever may be the acid and the base which react to form a salt, the same quantity of heat will always be developed per molecule of water formed, on condition that the reacting substances and the salt formed are completely dissociated. Otherwise it will be necessary to remove or supply heat to effect the ionic dissociation or the combination of the ions to form molecules.

The energy contained in the actual ions (*see* preceding footnote) is less than that contained in the potential ions (non-ionised substances). The molecules of chlorine gas contain much more energy than ionised chlorine, whilst, on the other hand, the difference in energy between $H^{\cdot}$ ions and the gaseous H_2 molecule is almost zero. We may consider the chlorine ion and the molecule of chlorine gas as allotropic forms of the same element, so that they should actually contain different quantities of energy. The heat of ionisation may be deduced in the following manner. It is found from various considerations, which we will not record here, that gaseous H_2 on passing into the ionised condition in solution would develop no heat; $H_2 + aq. = 2H^{\cdot}\,aq. +$ zero calories; the heat of formation of one molecule of hydrochloric acid in aqueous solution is 42,200 cals., that is, $H_2 + Cl_2 + aq. = 2H^{\cdot}Cl'\,aq. + (42200 \times 2)$ cals., and since the HCl is dissociated

---

chloride, is also present, a strong indicator should be employed and not phenolphthalein, because the $NH_4^{\cdot}$ cations of the dissociated ammonium salts fix a portion of the OH' anions of the strong base with which they unite even after the neutral point has been passed, ammonia and undissociated water being formed; thus, when using weak indicators, such as phenolphthalein, many OH' anions are required in order to repress dissociation, so that one obtains an uncertain titration, whilst strong indicators react immediately the neutral point is passed. If, on the other hand, the salt present contains a weak anion, it is advisable to use a weak indicator.

into its ions $2Cl'$ and $2H^{\cdot}$, and since also the ionic dissociation of hydrogen takes place without evolution of heat, the 42,200 cals. must be due exclusively to the ionic dissociation of the chlorine: $Cl_2 + aq. = 2Cl' aq. + 42,200$ cals. The heat of formation of chlorine ions in solution will then be equal to the heat of formation of HCl in solution, and in general *the heat of formation of any acid in dilute solution is equal to the heat of formation of its anions.* From the heat of formation of their salts, we may deduce the heat of formation of the metallic cations. On dissolving Na in HCl, NaCl is formed with evolution of H and of 57,100 cals. for each molecule of NaCl:

$$Na_2 + 2H^{\cdot}Cl' aq. = 2Na^{\cdot}Cl' aq. + H_2 + 2 \times 57100 \text{ cals.}$$

Since the $H^{\cdot}$ ions of the HCl do not develop heat on conversion into gaseous H_2, and the other new products of the reaction are only the $2Na^{\cdot}$ ions (for the chlorine ions already existed in the aqueous HCl), the 57100 × 2 cals. are due entirely to the formation of the $2Na^{\cdot}$ ions. Here also we may generalise and state that *when a metal reacts with an acid to form a salt and free hydrogen,* the heat developed depends only on the character of the metal and not on that of the acid, and corresponds with the heat of formation of the metallic cation.

DEGREE OF DISSOCIATION, EQUIVALENT AND SPECIFIC CONDUCTIVITY. Dissociation becomes more complete as a solution is diluted, and varies with the nature of the dissolved substance. Since the electrical conductivity increases with the number of ions, that is, with the number of dissociated molecules, we may measure the degree of dissociation of a substance in aqueous solution by measuring the electrical conductivity, also taking the mobility of the ions into account.

The energy of acids and bases is the greater, the more these substances are dissociated into the corresponding ions, and we may always determine it by means of the electrical conductivity. HCl is more energetic than H_2SO_4, and the latter more energetic than acetic acid, because if we take equal volumes of normal solutions of hydrochloric, sulphuric, and acetic acids, and mix them with similar weights of zinc, on collecting and measuring the hydrogen developed, it is observed that in equal times much more hydrogen is formed with the HCl than with the H_2SO_4, and still less with the acetic acid.

The velocity of reaction is different for the three acids, and we see that HCl reacts much more energetically than the other two and that different times are required for the evolution of all the hydrogen characteristic of these acids. If we measure the electrical conductivities of normal solutions of the three acids, we find that it is greatest in the case of HCl, less for H_2SO_4, and still less for acetic acid, and that the conductivities are exactly proportional to their velocities of reaction. But we know also that a solution conducts the electric current the more easily the greater the number of free ions, and the greater energy of reaction of HCl is explained as due to a larger number of free ions or of dissociated molecules. The strengths of bases may also be determined by the electrical conductivities of equivalent normal solutions.

In the case of polybasic acids, the dissociation is gradual in the same molecule; thus H_2SO_4 first dissociates into the two monovalent ions $H^{\cdot}$ and HSO_4', the anion HSO_4' being dissociated at a later stage into $H^{\cdot}$ and SO_4''.

The degree of dissociation (a) of various electrolytes, for equivalent solutions, is given by the ratio between the molecules which are dissociated into ions and those which are undissociated, and may be deduced in two ways, namely, from the osmotic pressure and from the electrical conductivity. We know that acids, bases, and salts in aqueous solution give abnormal osmotic pressures with respect to the molecular weights deduced by other methods, and we have seen that these abnormalities are due to the dissociation of molecules into ions. Van't Hoff indicated the coefficient which expresses how many times the molecular concentration resulting from osmotic determinations is greater than that theoretically deduced from the chemical formula, by the symbol i. If the fraction of dissociated molecules in 1 mol. of a given salt is denoted by a, and the non-dissociated portion of the molecules by $(1 - a)$, and if we also know the number, n, of the ions which the completely dissociated molecule is able to produce, the number of free ions is $n - a$ and the complete number of molecules and ions together, that is, i, will be: $i = 1 - a + na = 1 + (n - 1) a$, and the degree of dissociation, $a = \frac{i - 1}{n - 1}$.

Arrhenius, on the other hand, deduced the degree of dissociation from the electrical conductivity. He called the *specific conductivity*, k, of an electrolyte the current intensity set up when two electrodes, each of 1 sq. cm. surface, are immersed in the electrolyte 1 cm. apart and at a potential difference of one volt, and he compared this for different electrolytes, always referred to the same concentration, n, in equivalents per c.c. (normal solutions). (*See* the chapter on electro-chemistry for definition of the electrical units.) The *equivalent conductivity*, L, is then given by the formula, $L = \frac{k}{n}$. This equivalent conductivity increases with the dilution and tends towards the maximum conductivity, L_0, which corresponds with the complete dissociation of the molecule into ions, when all the ions take part in the transport of the current. It reaches this value only for infinitely dilute solutions, but for solutions of certain salts (KCl, NaCl, etc.) the maximum conductivity is shown for dilutions which are not very large and are easily measurable. In these cases the degree of dissociation, a, is given by $a = \frac{L}{L_0}$.

When the value of a is determined from the osmotic pressure (or the corresponding cryoscopic methods) and from the electrical conductivity, perfectly concordant values are obtained. It has thus been possible to group the various electrolytes according to their degrees of dissociation into (1) *strong electrolytes*, which are more than half dissociated, even in solutions of considerable strength, such as the alkali salts, the acids HCl, HBr, HI, HNO_3, HF, and H_2SO_4, the alkali and alkaline earth bases, the quaternary organic bases (but not ammonia), and (2) *weak electrolytes*, which are very slightly dissociated, such as the various salts of heavy metals with weak acids, ammonia, the non-quaternary organic amino-bases, and many weak acids, such as sulphydric, hydrocyanic, boric, carbonic, sulphurous, nitrous, hypochlorous, iodic, and phosphoric acids, and the organic acids.

It is then also found that the conductivity of solutions varies in proportion to the square root of their dilution. Thus, if a solution is diluted four times, its conductivity is reduced by half; if it is diluted ten times, the conductivity becomes 3·16 times less.

ISOHYDRISM AND IONIC EQUILIBRIUM. The ionic equilibrium in solutions of electrolytes may be influenced by various means, and since the dissociation of gases, for example, of the vapours of PCl_5 into $PCl_3 + Cl_2$, is repressed by addition of Cl_2 or PCl_3, so by the addition of one electrolyte to another having a common ion, the dissociation is influenced in a manner which is also regulated by the law of mass action (*see* p. 67).

When two electrolytes having a common ion are mixed and the concentrations of this ion are equal in the two solutions (*isohydric solutions*), no variation of the degree of concentration will take place even after mixing. If, however, two acids with different degrees of dissociation are mixed, the dissociation of both acids will be lowered, the change being much the greater with the weaker acid. The same remarks apply to bases and all weak electrolytes. In general, the further removed two solutions of electrolytes are from being isohydric, the greater will be the diminution of conductivity of the mixture compared with that of the original solutions.

In normal solutions of ammonia and acetic acid, the degrees of dissociation are 0·5 and 0·4 per cent. respectively. On adding to the first of these a normal solution of an ammonium salt and to the second a normal solution of an acetate, these values are reduced to 0·0022 and 0·0018 per cent. respectively. It is hence possible to diminish the acidic or basic properties of solutions of acids and bases very greatly, and this observation explains why, in presence of much ammonium chloride, magnesium salts are not precipitated by ammonia as magnesium hydroxide, and why the precipitation of zinc by means of hydrogen sulphide is prevented if a strong acid is added to the solution of the zinc salt so as to increase the concentration of the $H^{\cdot}$ ions and consequently to decrease the concentration of the sulphur ions of the weak precipitating acid H_2S. When wool is dyed in a bath acidified with sulphuric acid, the fixation of the dyestuff may be moderated by diminishing the acidity; such diminution of acidity and consequent retardation of the dyeing process are effected by adding sodium sulphate, which augments the concentration of the SO_4'' anions, and thus decreases the dissociation of the sulphuric acid.

MOBILITY OF THE IONS AND TRANSPORT NUMBERS. If we indicate the velocity which a cation acquires for a potential difference of one volt per cm. by u, and the corresponding relative velocity of an anion moving in the opposite direction by v, then, the charge of an equivalent-ion being always the same, viz., F coulombs (96,540 coulombs per gram-ion), it is clear that between the electrodes $u \,.\, F$ coulombs of positive electricity move each second with the cations and $v \,.\, F$ coulombs of negative electricity with the anions; the total current L_0 which is established will therefore be $L_0 = (u + v) \,.\, F$ coulomb-seconds or ampères. During this movement of the ions a certain number of cations will depart from the anode, and a certain number of anions from the cathode, so that in the proximity of the electrodes there will be a diminution of concentration, and by measuring this, per unit of time, we shall obtain an expression for the ratio of the velocities of the ions themselves. The ratio of the diminutions of concentration of the ions in the neighbourhood of the two electrodes represents, indeed, the ratio $\frac{u}{v}$. If from the variation in concentration of one of the ions in a given time we calculate how many coulombs have been transported by it, and then compare this number of coulombs with the total number passing through the electrolyte in the same time, we obtain the so-called *transport numbers*, which may be represented by the fractions $\frac{u}{u + v}$ and $\frac{v}{u + v}$.

For many salts in dilute solution the transport number is found to be about 0·5 (for KCl, for example, 0·497), and this signifies that half of the electric current is transported by the cation and the other half by the anion, so that the two have the same mobility. The transport number 1 would indicate that the whole of the current was transported by the anion or by the cation only, but this is never actually the case.

For dilute solutions of KCl, Kohlrausch calculated the equivalent conductivity L_0 to be, $L_0 = (u + v)\, 96540 = 130{\cdot}1$, and since the transport number for KCl, $\frac{u}{u + v} = 0{\cdot}497$, it is possible to calculate also the values of u and v, and from these, by taking into account the (maximum) equivalent conductivity, we may deduce the mobility of the ions of other salts.

The mobility of the $H^{\cdot}$ ions, characteristic of acids, is about five times that of the OH' ions, characteristic of bases, and about three times that of the more mobile ions of any other substance, and this explains why when equivalent solutions of strong electrolytes are compared, the acids and the bases show themselves much better conductors than the neutral salts, even if these latter are largely dissociated. In the case of electrolytes with polyvalent ions, the relations are more complicated, but for elementary ions in general the mobility is a periodic function of the atomic weight, whilst for complex ions it diminishes more or less regularly with increase of the number of the components of the ion.

At low temperatures all ions tend to acquire the same mobility.

COLOUR OF THE IONS. According to the electrolytic dissociation theory, the absorption of light by a completely dissociated electrolyte should represent the sum of the absorptions of the negative and positive components, so that the colour of a dilute solution depends on the colours of the free ions. Thus, all compounds containing colourless ions, *e. g.*, the cations $H^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $NH_4^{\cdot}$, $Zn^{\cdot\cdot}$, etc., and the anions Cl', Br', F', CN', NO_3', SO_4'', ClO_3', etc., are themselves colourless.

In salts the metallic cations determine the colour of the solutions, and with variation of the valency the colour of the ions also changes. Thus, $Fe^{\cdot\cdot}$ is green and solutions of all salts containing it (ferrous sulphate, chloride, etc.) will also be green; $Fe^{\cdot\cdot\cdot}$, on the other hand, is yellow, which is consequently the colour of solutions of ferric chloride, nitrate, etc.

As a rule, the ions composing electrolytes do not influence one another reciprocally and their specific characters occur in the most varied combinations. Thus Valson found that the difference in specific gravity between equivalent solutions of sodium and potassium chlorides is unchanged when the chlorine in these salts is replaced by another acid residue.

Ostwald's work on the absorption spectra of a series of salts of permanganic acid and of various coloured organic compounds led to the conclusion that the spectra of dilute solutions of various salts with ions of the same colour are identical. With permanganates ($MnO_4'X^{\cdot}$) in equivalent solution the colour does not change with variation of the metallic cation ($X^{\cdot}$), so that the coloration is due to the anion (MnO_4').

The colour of the undissociated salts may be the same as, or different from, the colour of the ions. The question of the equality or inequality of the absorption of light by the ions entered a new phase with the work of Hantzsch (and of Magnanini up to about 1892).

Hantzsch found that, in all cases, the coloration is influenced either not at all or but very little by the process of electrolytic dissociation with saturated co-ordinate compounds (*see* Werner's theory : chapter on cobalt).

The similarity in colour of copper sulphate and of its ions is explained by Hantzsch on the assumption that the absorbing part consists of the complex ($Cu^{\cdot}4H_2O$), which is found in both the undissociated molecule and in the ion.

Absorption spectra of coloured saturated co-ordinate compounds, *e. g.*, $(PtCl_6)'' Na_2$ and $[Co(NH_3)_6]^{\cdots}$, are influenced but little by change of temperature, solvent, or state of aggregation, provided always that the complex remains chemically unchanged.

IONS AND ELECTRONS. The ions are the so-called vehicles of the electric current and move without expenditure of energy (Clausius and Helmholtz), so that the negative current, which is transported by the anions (C', SO_4'', etc.), moves from the negative to the positive pole, that is, from the cathode towards the anode, whilst, on the other hand, the positive current passes from the positive pole (anode) to the negative pole (cathode).

The ions may be considered as minimal quantities of simple or compound substances corresponding with parts or fractions of molecules, and for each gram-ion and for each valency of these ions, a positive or negative electric charge of 96,540 coulombs is present. In the electrolysis of silver salts, for each coulomb 1·1181 mgrms. of silver are separated, and from the recent studies of Planck on the new law of radiation it has been found that one gram-ion of any substance contains a number of ions equal to $0{\cdot}617 \times 10^{24}$, that is, about half of a quadrillion; hence an ion of hydrogen weighs $1{\cdot}617 \times 10^{-24}$ grms. We can deduce from this that the quantity of electricity accompanying a free monovalent ion is $\frac{96540}{0{\cdot}617 \times 10^{24}}$, *i. e.*, $15{\cdot}63 \times 10^{-20}$ coulombs, whilst a divalent ion would have double, a trivalent ion treble this charge, etc. This smallest quantity of electricity which is known in the free state and accompanies the smallest quantity of matter (the monovalent free ion) is called the *electron.*

We have therefore *negative electrons* which are represented by the symbol $\overset{\frown}{\underset{\smile}{-}}$ and *positive electrons* represented by the symbol $(+)$, corresponding with the anion and cation of any dissociated substance, whilst in non-dissociated substances the two ions with their opposite charges are united and form the *neutron* $\overset{\frown}{\underset{\smile}{-}}\,(+)$. The degree of electrical conductivity of substances is thus dependent on the degree of dissociation of the neutrons. The neutrons of metals, for example, will be strongly dissociated, this explaining why they are such good conductors, and their rise in temperature during the passage of the current is due to friction between the electrons, because in the solid metal the solvent, which should serve as a sort of lubricant for the movements of the electrons themselves, as is the case in solutions, is lacking.

During electrolysis the ions which arrive at the electrodes separate neutral matter and the electrons which formed the electric charge of the ions are liberated and continue their course, detached from the matter with which they were at first joined, through the metallic wire of the circuit of the cell. Doubtless, however, the last word has not been said on the ultimate nature of electrons.

COLLOIDAL SOLUTIONS ("SOLS" AND "GELS")

We have already seen what important laws may be deduced from the study of *true dilute solutions*, and how van't Hoff established interesting relations between the osmotic pressure, the molecular weight and the pressure of the dissolved substances when these are in the gaseous state. We have seen how dissolved substances diffuse easily through the solvent, through other solutes, and also through partitions formed of various substances, more precisely of substances which do not follow the laws of van't Hoff and which are not electrolytes in the ordinary sense. There are, in fact, substances which yield aqueous solutions but exert no, or scarcely any, osmotic pressure, and thus have a minimal or zero power of diffusion, especially through membranes formed of substances of the same category. When solutions of these two different kinds are mixed, they may easily be separated again by introducing the mixture into a dialyser (*see below*); only that substance which has a high diffusive power will pass through the porous parchment membrane immersed in water.[1]

The classical studies of Thomas Graham (1862), which remained forgotten for a long time, have opened up during these later years a new horizon in connection with *dialysis*, by the explanation of certain industrial processes and by new applications which have recently been made and which we shall record later. Substances which diffuse through the dialyser often remain behind in the crystalline condition when the solvent is evaporated and re-form the original solution when mixed with the solvent. This process is, therefore, *reversible*, and such substances are called *crystalloids*. Those which do not diffuse are amorphous when the solvent is separated; they are analogous to glue and rarely re-form the original solution when mixed with the solvent. This is, therefore, an *irreversible process*, and these substances are called *colloids*.

As the osmotic pressure observed in colloidal solutions is extremely small we may infer that colloids have extremely large molecular weights, or at least we must assume that they form not true solutions, but *pseudo-solutions*, or suspensions of finely divided solids or liquids in another liquid. Graham called these pseudo-solutions *sols*, and, if they were formed in water, *hydrosols*. The substance which separates from a sol on elimination of the solvent, by heating, coagulation, or other means, was called a *gel*, or, if the solvent were water, a *hydrogel*. The phenomenon of the separation of the gel is called *gelatinisation* or *gelification*.

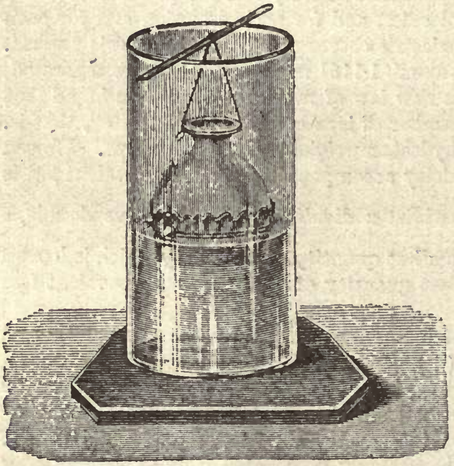


FIG. 33.

In the case of a very fine suspension of a solid in a liquid, the sol is called a *suspensoid*, whilst in the case of a very fine suspension of a liquid it is called an *emulsoid*. The latter are generally found already formed in nature (egg albumen, milk fat, etc.). Colloids in general may be considered as heterogeneous systems, the phases or components of which may be separated by physical means.

The dialyser (Fig. 33) which serves to separate colloidal from crystalline substances, is formed of a vessel the base of which is closed by a membrane of natural or artificial parchment. The mixture of the above-mentioned substances is poured into this and the vessel then partially immersed, in the case of hydrosols, in a second vessel containing water, which is renewed at intervals. After a certain time the crystalloid substance will have passed almost completely into the external water, and the aqueous colloidal solution will remain inside.

Hydrosols have all the external appearance of true solutions, as they seem perfectly homogeneous, may be filtered without leaving any solid residue on the filter, and show no discontinuity of the mass, even under the microscope. Nevertheless, they must be considered as heterogeneous systems for the following reasons: On allowing a colloidal solution to stand for a long time in a tall vessel the solution becomes more concentrated below, sometimes even forming a sediment, and becomes more dilute above; that is to say, through the influence of gravitation, one portion of the colloid is carried to the bottom, which would not be the case for a true solution. Metals have been pulverised under water

---

[1] This phenomenon of diffusion through a semi-permeable membrane cannot be considered as an exclusively mechanical action in which the membrane acts merely as a sieve and allows the smaller molecules to pass through its pores and not the larger ones. We must, on the contrary, assume a species of free selection by the membrane of the various substances which it allows to pass, by first dissolving them independently of their molecular size. Graham had already shown this in the case of gases. Thus, if a mixture of hydrogen and carbon dioxide is enclosed in a soap-bubble, the latter gas diffuses through the wall of the bubble because it is soluble in soap, whilst hydrogen does not diffuse although its molecules are much smaller, because it is only very slightly soluble.

by electrical means and hydrosols resulted. In this case, the idea that the metals are dissolved is excluded *a priori.* Finally, colloidal solutions offer a great resistance to the passage of the electric current, and the small conductivity which they show is due, not to a dissociation into ions, but entirely to the migration of a part of the colloid towards one of the electrodes. If they were true solutions, the boiling- and freezing-points would be different from that of the solvent, which is not the case.

On adding an electrolyte, for example an acid, to a hydrosol, a hydrogel is easily formed (that is, the sol is gelatinised), and this occurs with more or less ease in strict relationship with the dissociation constant of the electrolyte. Thus the action of salts on hydrosols is analogous to that they produce in fine mechanical suspensions, such as those of kaolin and ultramarine suspended in water. A colloidal solution of silicic acid is immediately coagulated by the addition of minimal traces of soda or by a few bubbles of carbon dioxide.

The material demonstration that hydrosols are mechanical homogeneous suspensions results, however, from an optical examination of these pseudo-solutions which shows that the Tyndall phenomenon[1] can be produced; further, by means of the ultra-microscope[2] we are able to see particles of a diameter of 5 $\mu\mu$ (*i. e.*, five one-millionths of a millimetre). Molecules of medium size have a diameter of about 0·6 millionths of a millimetre, and are not visible under the ultra-microscope.

A colloidal solution containing 2 mgrms. of gold per c.c. contains about one thousand million particles of suspended gold per cu. mm., that is, one trillion particles per c.c. The total surface of these particles is 625 sq. ms. per c.c., which explains the *catalytic action* of colloidal solutions.

The small suspended particles of hydrosols can be seen clearly with the ultra-microscope. They are endowed with a rapid zigzag movement similar to the *Brownian movement* and originating in the osmotic pressure. There are, however, other hydrosols, the suspended particles of which are still smaller than the limiting size which can be detected by the ultra-microscope, namely, less than 5 $\mu\mu$, so-called *amicroscopic particles.* Lobry de Bruyn and van Calcar subjected colloidal solutions to very powerful centrifugation, and found that the suspended particles accumulated at the circumference and not in the centre, which is a further confirmation of the heterogeneous nature of sols.

Since Rayleigh has found that the light reflected from very small material particles is of very short wave-lengths, Weimarn (1907) believes that still smaller particles, less than 5 $\mu\mu$ in size, could be detected by the ultra-microscope by illuminating the field by light rich in ultra-violet rays (by means of a fluorescent screen, or a mercury vapour or cadmium lamp).

The gas laws are applicable to Brownian particles (Iljin, 1913) and, by studying the movements of emulsions in pure water and in water containing glycerine and calculating

---

[1] If a luminous ray is concentrated with a lens into a true solution, freed from atmospheric dust by Spring's process, on observing the liquid in a direction perpendicular to the direction of the ray, the latter will be invisible. If, on the contrary, there are particles in the liquid which are suspended and not dissolved, even though they may be extremely small, these are illuminated by the luminous ray and disperse the light in every direction. In this case the observer will perceive light reflected from these luminous points, and this light will also be polarised. This is the Tyndall phenomenon. The suspended particles of colloidal solutions are not visible in this manner to the naked eye, but in 1903 Siedentopf and Zsigmondy reproduced the Tyndall phenomenon under the microscope, and the colloidal particles thus rendered visible are called ultra-microscopic particles, and their study in this way ultra-microscopy.

[2] The ultra-microscope of Siedentopf and Zsigmondy is an ordinary microscope under which an ordinary transparent object is observed, with, however, powerful lateral illumination. If the object is a true solution, and therefore perfectly clear, none of the rays will penetrate into the objective, and therefore the field appears quite dark, as the illumination is entirely lateral. If, however, there are solid particles in the solution, these collect groups of luminous rays and show refraction phenomena, so that certain luminous rays from the particles pass through the objective and arrive at the eye. The appearance is thus produced of a dark field sprinkled with luminous points (like a starry sky), which denote the existence of these particles indistinguishable by any other means. The phenomenon is, indeed, analogous to that observed when a ray of sunlight enters a dark or only slightly illuminated room, the whole of the luminous ray appearing filled by myriads of mobile corpuscles. These are due to the atmospheric dust, which is rendered visible under the influence of a powerful luminous ray, whilst when viewed in the ordinary way, even against the light of a window, it is not seen. The size of these particles varies from $\frac{1}{10000}$ to $\frac{1}{1000000}$, or even to $\frac{5}{10000000}$ of a mm. The particles exhibit Brownian movement, the cause of which is not known but which appears to some to present a case of perpetual motion, and thus of an exception to the law of the conservation of energy.

by means of Einstein's formula, Brillouin found the number of molecules in a gram-mol. to be 69×10^{22}. Further, it has also been shown that, no matter in what manner substances are decomposed, particles or molecules of the same size are always obtained. From the surface tension of liquids, Kleemann (1913) calculated the weight of a hydrogen atom to be $1{\cdot}56 \times 10^{-24}$ grams. From the modulus of refraction of the ions, Heydweiller (1912–1913) calculated the diameters of the ions to be as follows: H, $1{\cdot}65 \times 10^{-8}$ cms.; Na, $2{\cdot}07 \times 10^{-8}$ cms.; Ag, $2{\cdot}74 \times 10^{-8}$ cms.; Pb, $3{\cdot}42 \times 10^{-8}$ cms. and Cl, $2{\cdot}74 \times 10^{-8}$ cms.

Bredig and Billitzer assumed that the particles of hydrosols also carry an electric charge, though this is much smaller than that of ions. When an electric current is passed through a hydrosol the particles will be carried towards the anode or the cathode, according to their charge, in spite of the great resistance offered by the solution. The difference of electric potential between the suspended particles and the liquid medium in which they are present is in strict accordance with the surface tension of the liquid or medium which holds them in suspension. This potential difference may be greatly influenced by the addition of certain ions or electrolytes, as was experimentally shown by Hardy and Billitzer among others. Thus, if an electrolyte is added to a hydrosol a hydrogel is precipitated, and this absorbs a definite portion of the ions of the electrolyte—a portion of opposite charge to the particles of the hydrosol itself—forming a neutral gel.[1]

Lottermoser found that these hydrosols are stable only on condition that a certain number of ions are present to maintain equilibrium, so that the complete separation of the crystalloid from a colloidal solution by means of dialysis is not possible, because some of the ions of the former serve to maintain the colloid itself in the state of hydrosol. The presence of such ions in the hydrosol explains the electrical conductivity of the latter. Colloidal metals are generally transported to the positive pole, and thus carry a negative electric charge. Aluminium and iron hydroxides, on the other hand, go to the negative pole, and therefore carry a positive charge. It has been found possible to transform a hydrogel into a hydrosol by means of a solution of ions of definite concentration, corresponding with that necessary for the formation of the hydrosol. Thus Graham succeeded in transforming (*peptonising*) 200 grms. of a gel of silicic acid into a hydrosol by heating it for sixty minutes at 100° with a solution of one part of NaOH in 10,000 parts of water. In the same way gelatinised ferric hydroxide or aluminium hydroxide may be peptonised by means of small traces of hydrochloric acid.

If two hydrosols carrying equal electrical charges of opposite sign are mixed, they are mutually precipitated. This explains the great gelatinising power of certain salts with polyvalent cations (even in small quantity) on negatively charged hydrosols. On the other hand, salts with monovalent cations need to be added in much larger quantities in order to produce the same gelatinisation. Certain polyvalent cations have a precipitating power (separation of gel) a thousand times greater than that of monovalent cations. If hydrosols of equal electrical charge of the same sign are mixed no gelatinisation takes place, but the mixture has properties different from those of the individual components, as may be shown by its different behaviour towards electrolytes. In fact, the properties of that component which is more stable with respect to electrolytes predominates in the mixture, and thus, whilst the red gold hydrosol becomes blue on adding an electrolyte, when it is mixed with the hydrosol of stannic acid the addition of an electrolyte still causes the separation of the gel, but the properties of the stannic acid alone are changed and not those of the gold, which retains its red colour in the gel. We may thus say that the stannic acid hydrosol has a protective action on that of gold, and similarly when certain organic hydrosols (false hydrosols) not gelatinisable by electrolytes are mixed with true hydrosols, which are gelatinisable, they exercise a protective action to such an extent that the

---

[1] Billitzer believes that each suspended particle of a hydrosol is accompanied by a definite quantity of water in a state of latent dissociation (hydrolysis), and according to whether this discharges $H^{\bullet}$ or OH' ions into the solution we have particles of positive or negative character. The actual precipitation of hydrosols in the form of gels by the action of electrolytes appears to be due to the union of cations or anions of the electrolyte with the anions OH' and cations $H^{\bullet}$ accompanying the particles of the hydrosol to form neutral molecules. However, free ions of $H^{\bullet}$ or OH' remain, and thus the solution acquires an acid or basic character. If we have, for example, a hydrosol with negative particles, the latter (OH' anions) will unite with the cations of the electrolyte added (for example, a salt) and the neutral gel will separate, but free $H^{\bullet}$ cations of the hydrosol will remain after hydrolysis has occurred, and the liquid will acquire an acid reaction. This fact has been actually confirmed in practice in the case of various reactions of colloidal solutions.

gelatinisation of the two by the addition of electrolytes is prevented. These substances are called *protective colloids*,[1] and are capable of transforming irreversible inorganic colloids —that is, those with gels not retransformable into sols—into reversible colloids, and use is made of this fact in medicine in order to retain in solution certain colloids which greatly affect the human organism (collargol, etc.).

Thus colloids possess the two following fundamental properties: (1) they absorb reagents (*e.g.*, water) in irrational proportions; (2) they retain the absorbed substances without forming chemical compounds with them. The absorbent and absorbed substances preserve their original properties and in certain cases the process of absorption is reversible. An important example of absorption is furnished by the weighting of silk (*see* Vol. II., "Organic Chemistry").

The general conditions favourable to the formation of hydrosols may be summarised as follows. Solutions in which hydrosols are to be formed should be free from polyvalent ions of contrary charge, and the concentration of the monovalent ions should not exceed the limiting value above which they cause the formation of a gel, that is, in general very dilute solutions are required. Other hydrosols may be obtained by acting on colloids with solutions of electrolytes which give a reversible precipitate, that is, one capable of being reconverted into a hydrosol by the simple action of water. The use of protective colloids facilitates formation of hydrosols, even if the concentration limit of the electrolytes present is exceeded.

Bredig, and later Billitzer, have obtained hydrosols of the noble metals by dispersing them by means of the electric spark, under water, and the sols of other metals by employing indifferent organic solvents (organosols). In the latter cases it is not possible to obtain hydrosols because these metals decompose water when so finely subdivided.

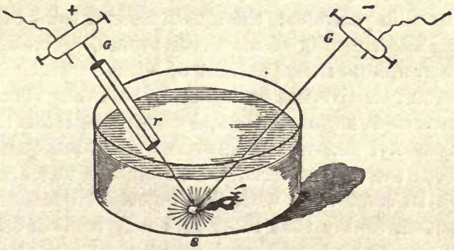


FIG. 34.

In order to prepare a hydrosol of gold, Bredig's arrangement may be used (Fig. 34). In a vessel, *S*, of about 100 c.c. capacity, cooled externally with ice, purest distilled water containing a trace of sodium hydroxide (0·01 grm. of normal NaOH) is placed. 2 cms. below the surface of the water are two electrodes of gold wire, *G*, of about 1 mm. diameter; the points of these are brought nearly into contact, a current of 8 to 10 ampères at 100 volts is passed, and the points are then separated from one another by 1 to 2 mm. and moved in such a manner that small voltaic arcs are formed which give a peculiar hissing sound. It is more especially the cathode which is then dispersed, forming extremely fine particles which pass through filters and give a deep red colloidal solution which remains unchanged on standing even for two years.

A colloidal solution of gold is more easily obtained by dissolving 15 mgrms. of crystalline gold chloride and 0·6 grm. of potassium bicarbonate in 125 c.c. of pure water (distilled through a silver coil). On boiling this liquid and then adding 0·01 c.c. of commercial formaldehyde, an intensely red solution of colloidal gold is obtained, which is very sensitive to electrolytes. Colloidal solutions of ferric hydroxide are obtained by dissolving the hydroxide in ferric chloride and then eliminating the latter by dialysis. A colloidal solution of silicic acid may be obtained by treating a concentrated solution of sodium silicate with hydrochloric acid and then eliminating the sodium chloride and excess of hydrochloric acid with water in a dialyser.

---

[1] The casein of milk is present as an irreversible hydrosol, and its coagulation by means of an acid or of heat may be retarded or prevented, or caused to yield more or less fine and subdivided flocks, by the presence of reversible or protective colloids, such as gelatin, gum, albumen, etc. In cow's milk the ratio of the irreversible casein to the reversible albumen is as 3·02 : 0·53. The larger quantity of reversible albumen in human milk (0·75 : 1·00) renders its coagulation eight times more difficult than that of cow's milk, and the finer coagulum which is obtained explains its greater digestibility and assimilation in the stomach of a child, and also explains why, without suitable treatment, cow's milk cannot be substituted for human milk with impunity for the artificial feeding of infants.

Zsigmondy has called the number of milligrams of a protective colloid necessary to prevent the precipitation of 10 c.c. of a red gold hydrosol by the addition of 1 c.c. of a 10 per cent. solution of sodium chloride, the *gold number*.

Ethereal sols of the alkali and alkaline earth metals are variously coloured (blue, violet, green, etc.) according to the size of the particles.

The theoretical and practical applications which have resulted from the study of colloidal solutions are much more numerous and important than might appear.

The far-famed production of ruby glass is a phenomenon of this kind. If to a glass paste which is molten or half molten but not too hot, and which may be considered as a solvent with almost infinite viscosity, a gold salt (chloride) is added, this is decomposed, and very fine (amicroscopic) particles of gold remain in the glass. If the latter is cooled rapidly a transparent, colourless glass is obtained. If, however, the pasty mass is heated to a certain temperature so that it becomes more fluid, the gold particles, having less friction to overcome, are enabled to move and to reunite to larger particles, thus imparting to the glass a whole series of successive colorations from violet, through purple to ruby, red, pink, etc.; this method is used in practice to obtain the various coloured glasses, even with as little as 0·05 per cent. of gold.

If the glass paste is heated to still higher temperatures, through a mistake of the operator in not hitting the exact point, the particles unite to form larger and easily visible aggregates which give to the glass the true reflex of metallic gold. In the case of glasses rendered milky by calcium fluoride and of enamels coloured by means of metals, similar phenomena occur. Various precious stones owe their brilliant colorations to colloidal metallic particles; the amethyst is a solid colloid, and the opal a solid gel of silica.

The ripening of the silver bromide-gelatine plate in photography is also due to a slow regrouping of the particles of bromide which is indispensable in order to obtain the maximum sensitiveness to light. In ceramics the ripening of the paste of kaolin or clay, which renders it more plastic and sometimes takes three months, is due to the action of alkaline hydroxyl ions which peptonise the small quantity of colloidal organic substances derived from the raw materials and from the water with which the paste is prepared.

In connection with the important question of the purification of effluent waters, it is known to-day that these generally contain extremely fine suspensions of electro-negative character and are therefore easily precipitated by the addition of polyvalent cations, for example, of ferric salts. (In certain towns this system has been applied, *see* Water.)

The action of bacteria in the biological process of sewage purification (*q. v.*) appears to be due partly to the formation of colloids of opposite electric charge to that of the organic suspensions in the water, so that they are reciprocally precipitated.

In the formation of metallic filaments for the manufacture of incandescent electric lamps it has been found that tungsten, for example, which melts at 2800°, is insufficiently ductile to render it possible to prepare sufficiently fine and regular filaments. When, however, tungsten separated from a colloidal solution is used, regular filaments of a diameter of 0·03 mm. are easily obtained.

The setting and hardening of cement is now explained by the formation of gelatinised silica and alumina, which surround the crystals of calcium hydroxide and aluminate, thus forming a compact mass protecting these from the action of water and of ordinary reagents.

In arable soil various phenomena of colloidal character also occur.

Many of the phenomena connected with the tanning of hides, the dyeing of textile fibres, etc., are colloidal actions. Vegetable and animal life is also largely based on reactions between colloids and crystalloids in the cell. Amongst catalytic actions of colloids, we may mention that of a colloidal solution of platinum which causes the combination of H and O, even in the cold; a colloidal platinum solution containing only $2{\cdot}8 \times 10^{-6}$ grams of the metal is capable of decomposing hydrogen peroxide. The catalases of the blood, which are colloidal enzymes, cause the passage of the oxygen from the oxyhæmoglobin into the tissues, and also cause decomposition of hydrogen peroxide with liberation of oxygen; by means of the latter reaction we may determine the richness of the blood in catalases and decide if the organism is in a normal condition or not. Bredig has obtained these enzymic effects (catalysis) with colloidal solutions of platinum, and such colloidal metallic solutions, which produce numerous and important catalytic phenomena, he calls inorganic ferments. He also found that substances which have a poisonous action on the animal organism, such as hydrocyanic acid, hydrogen sulphide, corrosive sublimate, arsenic, etc., likewise behave as poisons towards colloidal solutions, completely paralysing their action.

MATTER IN THE SOLID STATE

It is supposed that the molecules of solids are placed very close to one another compared with those of liquids, and that their distance and relative position always keep constant, though they perhaps remain endowed with oscillatory movement. The sum total of the kinetic energy of these molecular movements is less than that in the same substances in the liquid state; hence, on lowering the temperature of liquids, and so abstracting energy, they have a tendency to solidify.

When pure, simple or compound solid substances are often characterised by their melting-point, this being determined in various ways which are described in treatises on practical physics, and for organic substances will be explained in the second volume.

SPECIFIC GRAVITY OF SOLIDS

The specific gravity of solids is the relation between the weight of a given volume of the solid substance and the weight of an equal volume of water at 4°.

There are many ways of determining the specific gravity: by measuring the volume of water which a given weight of a solid displaces when immersed in the liquid contained in a graduated vessel; or by determining the weight of water or other liquid of known specific gravity displaced from a filled pyknometer by a given weight of the solid substance under examination. This method cannot be used when the solid substance is soluble or if it sucks up the liquid (water, oil, alcohol, etc.) into its pores when immersed.

In such cases so-called volumenometers are employed, which are based on the difference in dilatation of air contained in a given volume before and after the introduction of the body under examination.

A fourth method consists in the immersion of the solid substance in a liquid to which soluble substances of greater density are added until a solution is obtained in which the body under examination just floats. In order to know the specific gravity of the solid substance, all that is necessary is to determine that of the solution (*see* p. 75), which will be identical with the former. This method is exact, and is employed not only in laboratories, but also commercially, to ascertain, for example, if eggs are fresh or potatoes ripe, to determine the starch-content of potatoes, etc.

SPECIFIC HEAT OF SOLID SUBSTANCES

In order to heat the same weight of different substances to the same temperature, different quantities of heat are required. On heating 1 kilo of lead and 1 kilo of zinc to 150° and then immersing them separately in equal volumes of water, for example, one litre, the water in which the zinc is immersed becomes much the hotter. The physical unit for heat measurements is the calorie (*see* Thermochemistry).

The *specific heat* of a substance is defined as the quantity of heat required to raise the temperature of 1 kilo of the substance from 0° to 1°.[1] It is determined by means of very exact forms of apparatus called calorimeters, in the following manner:

The weighed substance is heated to a definite temperature and allowed to fall into the calorimeter (*see* chapter on carbon and fuel), containing a measured quantity of water of which the initial temperature is noted. The water is stirred, and when its temperature no longer rises, the rise of temperature which has occurred is read on the thermometer, and by correcting the results for the constant quantity of heat absorbed by the calorimeter, all the data for calculation of the specific heat are obtained.

---

[1] *See* Table on following page.

In 1818 Dulong and Petit found, from a long series of determinations, that the specific heat of an elementary substance is smaller the larger the atomic weight, and they discovered the following law which bears their names: *the specific heats of solid elements are inversely proportional to their atomic weights*, that is, the atoms of the solid elements have the same thermal capacity. Thus, on multiplying the specific heat, C, by the atomic weight, A, we obtain a constant value for all the solid elements. The following table completely explains and confirms this law:

		Iron	Copper	Silver	Iodine	Gold	Bismuth
Specific heat (C)	=	0·114	0·095	0·057	0·054	0·032	0·030
Atomic weight (A)	=	55·9	63·6	108	127	197·2	208·5
Atomic heat ($C \times A$)	=	6·40	6·00	6·15	6·80	6·31	6·20

As we see here, the specific heats of elements diminish as their atomic weights increase, and the product of the atomic weight (A) and specific heat (C) is almost constant. This constant, which is called the *atomic heat*, has been found by means of many direct determinations to have a value approximating to 6·4.

This law is demonstrated sufficiently well by the very simple experiment illustrated in Fig. 35. Two rings of equal weight of zinc, *a*, and of lead, *a*, weighing, say, 1 kilo, are heated to the same temperature in an oven and then immersed in two beakers containing equal quantities of water; this will then be heated to different temperatures. This difference of temperature is easily made evident by immersing in each of the beakers of water a thermometer, formed of a test-tube containing at the bottom a little coloured liquid into which dips a long glass tube, secured by a stopper. The hotter water causes the air contained in the chamber of the one improvised thermometer to expand more than that in the other, and the coloured liquid will therefore rise to a greater height in the tube. In this case the thermometer will naturally give a larger indication in the case of the zinc, because the atomic weight of this is the less, and the specific heat is, therefore, the

SPECIFIC HEAT OF VARIOUS SOLIDS (WATER = 1).

Substance	Temperature of experiment	Specific heat	Substance	Temperature of experiment	Specific heat
Aluminium	from 15°–185°	0·2189	Selenium, amorphous	21°–57°	0·1125
Antimony	,, 0°–100°	0·0486	Silver	0°–100°	0·0559
Lead	,, 20°–100°	0·0304	,,	at 700°	0·0590
,, liquid	at 360°	0·0402	Zinc	20°–100°	0·0931
Calcium	0°–100°	0·1804	,,	300°	0·1040
Chromium	0°	0·1039	Tin	20°–100°	0·0551
,,	100°	0·1121	Various bronzes	—	0·1043
Iron	23°–100°	0·1162			0·0874
Cast iron	0°	0·1050	Brass	—	0·0743
,, ,,	75°	0·1136			0·0873
Gold	0°–100°	0·0316	White metal	—	0·0946
Potassium	— 78 to + 23°	0·1662	Alumina, Al_2O_3	0°–100°	0·1879
Cobalt	10°–100°	0·1067	Lead oxide	20°–50°	0·0553
,,	at 800°	0·1845	Iron oxide, Fe_3O_4	24°–100°	0·1678
Coal	24°–68°	0·2040	Sodium hydroxide	0°–98°	0·780
Wood charcoal	0°–100°	0·1935	Quartz	12°–100°	0·1881
Graphite	10°	0·1604	Rock salt	0°	0·2146
,,	200°	0·2966	Iron sulphide, FeS_2	0°–100°	0·1459
,,	977°	0·4670	Gypsum, crystallised	0°	0·254
Diamond	10°	0·1128	Sodium sulphate	17°–98°	0·2312
,,	200°	0·2730	Potassium nitrate	14°–45°	0·232
,,	985°	0·4589	Marble	22°–100°	0·212
Copper	20°–100°	0·0936	Mica	20°–100°	0·2070
Magnesium	18°–99°	0·2460	Ice	— 78 to 0°	0·4627
Nickel	20°–100°	0·1084	Mirror glass	10°–50°	0·1860
,,	500°	0·1233	Portland cement (clinker)	28°–40°	0·186
Platinum	18°–100°	0·0324	,, ,, (set)	28°–30°	0·271
,,	100°	0·0409	Cellulose	—	0·366
Mercury	20°–50°	0·0331	Paraffin wax	0°–20°	0·694
,,	250°	0·0321	,,	52°–55°	0·700
Sulphur, rhombic	17°–45°	0·1630	Wool, dried	—	0·393
,, liquid	119°–147°	0·2346	,, + 11 per cent. water	—	0·459
Selenium, crystallised	22°–62°	0·0840			

greater. If, on the other hand, quantities of zinc and of lead proportional to their respective atomic weights are taken, the water in the two vessels will be heated to an equal extent.

If the atomic heat is constant for all the elements, we have a new method for determining the atomic weights of the solid elements by simply determining their specific heat, because $A = \frac{6{\cdot}4}{C}$; on the other hand, knowing the atomic weight of an element, we are also in a position to know its specific heat, since $C = \frac{6{\cdot}4}{A}$.

Regnault confirmed the law of Dulong and Petit generally by a long series of experiments (1840–1855). He observed, however, that silicon, boron, and carbon do not follow this law and give very low atomic heats. This abnormality could not be explained for some years and these elements were considered as true exceptions, but in 1875 H. F. Weber, of Zürich, found an explanation for this anomalous behaviour. He found that the specific heats of these three elements vary greatly with the temperature at which the determination is carried out and that the atomic heats increase on elevating the temperature. Thus, whilst at 10° carbon showed a specific heat corresponding with an atomic heat of 1·35, at 1000° the atomic heat is 5·6 and is thus very near to the thermal constant, 6·4. The same fact was demonstrated for boron and silicon (at 1200°).

It has now been clearly shown that the specific heat of solid and liquid substances diminishes greatly with fall of the temperature and tends to a value approximating to zero at the absolute zero of temperature.[1]

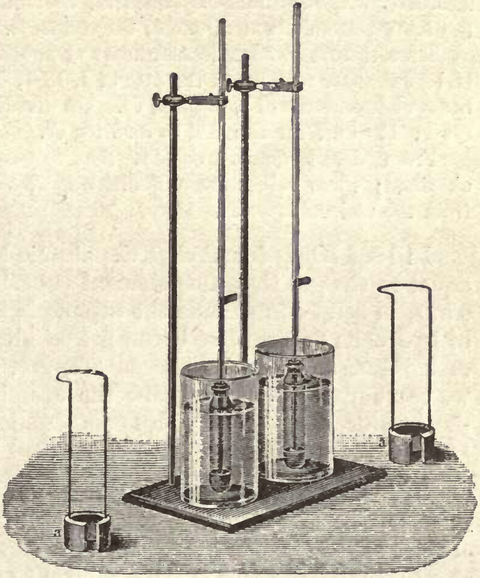


Fig. 35.

In 1831 Neumann found that stoichiometric or equimolecular quantities of compounds which have analogous chemical composition have equal thermal capacities (molecular heats); this is the case, for example, with the metallic perchlorates, ClO_4M, and permanganates, MnO_4M, and with the metallic nitrates, NO_3M, and metaphosphates, PO_3M, etc., where M indicates the atom of a metal.

Joule in 1844 and Woestyn in 1848 showed that the thermal capacity of chemical compounds (molecular heat) is equal to the sum of the thermal capacities of their components (or atomic heats), and this was confirmed by Regnault and Kopp. This law obviously includes that of Neumann.

Hence, the molecular heat ($C \times M$) of a compound is equal to the calorific constant multiplied by the number of atoms which the compound contains: $C \times M = 6{\cdot}4 \times N$, where N is the number of atoms and M the molecular

---

[1] Kamerlingh Onnes has studied the physical behaviour of substances at temperatures approximating to absolute zero. A narrow column of mercury a metre in length showed a very slight but still appreciable electrical resistance at − 268·7°, but lost its resistance completely at − 271·3°, so that a current of 1000 ampères per sq. mm. of section passed without any potential difference being detectable at the ends of the column, and hence without any development of heat. Such temperature, in absolute or Kelvin degrees, is 1·7° for mercury, 3·8° for tin, and about 6° for lead. The parallelism between the electrical conductivity or resistance and the specific heat is hence evident.

weight. This is fully confirmed by experience, as is seen in the following examples:

I. Specific heat of PbI_2 = 0·0427; molecular weight (M) = 459·4; number of atoms = 3
lead iodide
II. ,, ,, $PbBr_2$ = 0·0533; ,, ,, ,, = 365·9; ,, ,, = 3
lead bromide
III. ,, ,, $PbCl_2$ = 0·0664; ,, ,, ,, = 277·1; ,, ,, = 3
lead chloride

The specific heat being inversely proportional to the molecular weight, $C \times M$ = constant (molecular heat) for analogous compounds.

In the three examples cited above, we in fact find almost equal molecular heats, namely, I = 20·1; II = 19·9; III = 18·4.

Knowing the molecular constant or molecular heat, we may deduce the atomic heat by dividing by the number of atoms; in our case, by dividing by 3, we obtain, I = 6·70; II = 6·67; III = 6·13. We may also calculate the atomic heats of these elements indirectly without direct experimental determination by using the molecular heats and the known atomic heat of one of the elements.

Thus, if from these molecular heats we subtract the atomic heat of lead, which is known to be 6·5, there remains in the case of I, 13·6; II, 13·40; III, 11·90, which are the atomic heats of two atoms of I, Br, and Cl. On dividing these numbers by 2, we obtain, I = 6·8 for I; II = 6·7 for Br; III = 5·95 for Cl.

From direct determinations, the values, iodine = 6·86 and bromine = 6·74, are obtained; these values are in sufficiently close accordance with those indirectly deduced from the molecular heats.

In 1864 Kopp found that the atomic heat of the free elements is not always equal to that of the same element contained in different chemical compounds. Thus, in solid compounds the atomic heat of carbon is always about 1·8, that of hydrogen 2·3, that of boron 2·7, of glucinum 3·7, of silicon 3·8, of oxygen 4, of sulphur 5·4, of phosphorus 5·4, etc. Taking these values into account, we can equally well determine the atomic weight of an element if we know the specific heat of one of its compounds.

A practical example will suffice to illustrate the method of determining the atomic weight of an element, for example, of calcium, by the method of specific heats. Analysis shows that 1 kilo of calcium carbonate, which has a thermal capacity of 0·202, is composed of 0·400 kilo of calcium + 0·120 kilo of carbon + 0·480 kilo of oxygen. The atomic heat of carbon in combination is 1·8, and dividing this value by the atomic weight we obtain as the specific heat of carbon $\frac{1·8}{12} = 0·15$, and therefore the thermal capacity of 0·120 kilo of carbon will be $0·120 \times 0·15 = 0·018$. For oxygen, with an atomic heat of 4 and an atomic weight of 16, we arrive at the specific heat $\frac{4}{16} = 0·25$, and the thermal capacity of 0·480 kilo of oxygen will be $0·480 \times 0·25 = 0·120$; on deducting the thermal capacities of carbon and oxygen $(0·018 + 0·120 = 0·138)$ from the thermal capacity of 1 kilo of calcium carbonate = 0·203, we have the thermal capacity of 0·400 kilo of calcium $= 0·203 - 0·138 = 0·065$, and thus the specific heat of calcium will be $\frac{0·065}{0·400} = 0·162$. Having thus indirectly found the specific heat of calcium in combination, and knowing that calcium, being a metal, will certainly have a normal atomic heat of about 6·4, we may deduce the atomic weight of calcium by dividing the atomic heat by the specific heat, that is, $\frac{6·4}{0·16} = 40$.

By the analysis of many calcium compounds, its equivalent has always been found to be 20·05, and since we know that the atomic weights are equals or multiples of the equivalents, therefore the atomic weight of calcium will be 40, that is, double the equivalent.

The method of determination of atomic weights by means of specific heats is now very little used, because there are so many other methods which are more exact and convenient, but this method may always be employed as a check and serves also for substances which cannot be evaporated or dissolved. The law of Dulong and Petit is fairly exact for elements which have an atomic weight greater than 35.

MATTER IN THE CRYSTALLINE STATE[1]

ISOMORPHISM. Before 1800 the law of Hauy was generally believed, which said that a given substance corresponded with a given crystalline form, and that different substances had different crystalline forms, but in 1798 Klaproth showed that aragonite, which is rhombic, and calcite, which is hexagonal, have different crystalline forms, although they have the same chemical composition, $CaCO_3$. Hauy endeavoured to explain this observation by attributing it to impurities in these substances, but in 1807, Thénard and Biot showed that there is absolutely no chemical difference between aragonite and calcite (calcspar). Numerous substances of different chemical composition and the same crystalline form were found later, and in 1815 Fuchs advanced the idea that in the same crystalline form certain elements can be replaced by others. It was only through the work of Mitscherlich (1820–1823) that light was thrown on this question, and his numerous and exact experiments showed with certainty that compounds of analogous chemical composition have the same crystalline form, that is to say, are *isomorphous*. A given chemical substance may, however, crystallise in more than one system (according to the conditions of temperature, concentration, etc.), and such substances are spoken of as *polymorphous*—thus calcium carbonate is *dimorphous*.

Through the phenomenon of isomorphism the possibility thus arises of controlling the molecular weight or chemical formula of a given compound when the formula of an isomorphous compound is known. Generally speaking, isomorphous compounds contain the same number of atoms (or groups of atoms which are equivalent to these).

By means of the conception of isomorphism, we may consider as the atomic weight of an element that quantity which is equivalent to or may substitute the atom of another element in their respective isomorphous compounds. In the case of calcium, for instance, which does not yield volatile products, we may deduce its atomic weight by means of the isomorphism of many of its compounds with analogous magnesium compounds, and those atomic weights of calcium, barium, and strontium have been accepted which express the quantities of these metals which are able to replace 24·4 parts of magnesium, that is, an atom of magnesium, Mg.

Isomorphous substances may be superposed in layers in the formation of a single individual crystal, and thus, if a white octahedral crystal of potash alum is placed in a solution of chrome alum under suitable conditions as to temperature, concentration, etc., it continues to enlarge homogeneously, and we thus obtain a new, coloured, reddish layer formed by the enlargement of the same octahedron. We may invert the operation, superposing the white layer of potash alum and may then superpose other strata of various other isomorphous alums.

---

[1] Nicola Steno in 1669 was the first to note the regularity and constancy of the angles between the faces of a crystal, and was followed later in 1783 by Romé de l'Isle, who was the first to adopt exact instruments for measuring angles. Hauy, from 1781 to 1801, studied the relations between the angles of a crystal and of its faces with regard to its axes, and he established the law that each substance has a definite crystalline form and that substances of different composition have different crystalline forms.

The path of modern crystallography was first pointed out in 1809 by Weiss, who established rational conceptions regarding the axes and referred the different crystalline forms to these. Various mathematicians, and more especially F. Neumann, perfected and developed these conceptions, and arrived at six fundamental crystalline systems to which all the innumerable crystalline forms now known are referred, and these studies form the subject of crystallography (*see* succeeding Note).

We here give the formulæ of a series of isomorphous alums which have the same crystalline form:

Potassium aluminium sulphate = $AlK(SO_4)_2 + 12\ H_2O$
Sodium ,, ,, = $AlNa(SO_4)_2 + 12\ H_2O$
Ammonium ,, ,, = $Al(NH_4)(SO_4)_2 + 12\ H_2O$
Potassium ferric sulphate = $FeK(SO_4)_2 + 12\ H_2O$
Potassium manganese sulphate = $MnK(SO_4)_2 + 12\ H_2O$
Potassium chromium sulphate = $CrK(SO_4)_2 + 12\ H_2O$

By analysing these alums we may deduce the atomic weight of an element which is replaced in an alum by another element, on the analogy of the formulæ of the various alums.

It is not very easy to decide by their external appearance whether two substances or two crystals are isomorphous. A safer opinion may be arrived at by mixing the two substances together and then crystallising them. We should then be able to separate so-called *mixed crystals*, that is, crystals of a single form, but simultaneously containing varied proportions of the two substances, the particles of which are not separable by any mechanical means and are not individually perceptible, even when the crystals are finely crushed. Also on melting solid isomorphous substances together, mixed crystals separate. Van't Hoff called the substances of which these mixed crystals are composed *solid solutions*, on account of the analogy which exists between them and ordinary liquid solutions, although the cryoscopic laws cannot be applied to them because the pure solvent does not separate as ice, as is the case in ordinary dilute solutions.

Potassium perchlorate, the formula of which is well known to be $KClO_4$, is isomorphous with potassium permanganate, and if we wish to determine the atomic weight of manganese we commence by determining the equivalent of manganese in various substances. This is found to be 55, and in all analyses potassium permanganate is found to contain 39 parts of potassium (one atom) corresponding with 64 parts of oxygen (four atoms). The permanganate being isomorphous with potassium chlorate, its formula must be $KMnO_4$, that is, the equivalent 55 corresponds with a single atom of manganese, so that the atomic weight of the latter will be 55, and not a multiple of this number.

From the study of isomorphism, Roscoe was enabled to find the atomic weight of vanadium; it was possible also to deduce with certainty the atomic weight of chromium and to establish the formula Fe_2O_3 for ferric oxide on account of its analogy with chromium oxide, which certainly has the formula Cr_2O_3.

There are certain substances which have perfectly analogous chemical compositions, but do not crystallise in the same system even when pure. Thus, for example, magnesium sulphate when pure always crystallises in rhombic prisms of $MgSO_4$, $7H_2O$, whilst pure ferrous sulphate always crystallises in monoclinic prisms, $FeSO_4$, $7H_2O$.

These substances, however, when mixed in solution have the property of forming mixed crystals containing the two substances. If magnesium sulphate preponderates in the solution these crystals are exclusively rhombic prisms, but when the ferrous sulphate predominates, the crystals are exclusively monoclinic prisms. This important phenomenon is termed *Isodimorphism*, and such substances are called *Isodimorphous*.

Isodimorphism has to-day lost its former importance for the determination of atomic and molecular weights, because other much more convenient, exact, and certain methods have been discovered. The isodimorphism of certain compounds has even led previous workers astray. Thus calcium carbonate, $CaCO_3$, which, as we have seen, is dimorphous, presents the same crystalline form when in the state of calcite as sodium nitrate, $NaNO_3$, and when present as aragonite has the same form as potassium nitrate, KNO_3.

LIQUID CRYSTALS. At first sight the existence of liquid crystals may seem strange if we refer the expression to the common definition of crystals and of liquids. If, however, we consider crystals from a more general and rigorous point of view, we may easily understand how there may even be liquid crystals.

In 1888 Reinitzer observed that certain pure substances melt unaltered, forming a turbid liquid, and at a higher temperature, which is well defined, they again become clear. On recooling these liquids, the first turbid liquid is reproduced and is then followed by solidification. Gattermann observed the same behaviour in certain substances, for example, para-azoxyanisol, which melts at 116° giving a yellowish turbid liquid which immediately becomes clear at a temperature of 135·2°. O. Lehmann, and R. Schenck somewhat later, found that these turbid liquids light up the dark field obtained between crossed Nicol prisms precisely in the same way as crystals, a property not shared by true homogeneous liquids.

Tammann, and to a certain extent Nernst, pointed out that this apparently strange phenomenon could be explained by the theory of emulsions or of partial polymerisation, or even by the formation of isomerides of the substance observed. Weimarn in 1909 stated that under the ultra-microscope these special liquids showed the presence of small crystals which were already formed. In any case this matter has not yet been definitely cleared up, and it may be considered premature to suggest that the origin of life was initially due to the formation of liquid crystals ![1]

[1] It has often been affirmed that the characteristic properties of the crystalline state of a substance are anisotropy and perfect homogeneity at all points in the mass. Substances are called anisotropic which do not possess the same vectorial properties in every direction. Thus, the double refraction of crystalline substances is due to vectorially discontinuous properties. Amorphous substances have vectorially continuous properties and they are not doubly refractive. Crystalline matter, in distinction from amorphous matter, has generally regular planes of cleavage, and these are the ones which also establish the constancy between the angles of crystalline faces when the mass is limited by faces and assumes regular geometrical forms.

It cannot be denied, however, that sometimes even amorphous substances are anisotropic, that is, doubly refractive; for example, a sheet of gelatine, a starch granule, a piece of tempered or compressed glass, animal hide, etc., although as a whole they are isotropic and may be considered as consisting of small anisotropic particles only. Thus a piece of tempered glass, which is not homogeneous, may always be imagined to consist of small isolated particles in which it is no longer possible to distinguish two points arranged differently in respect to the optical ellipsoid; however, in this case we must admit that the more intimate arrangements of the particles of these substances may be a network such as is present in crystalline substances. In amorphous substances, however, the phenomenon of cleavage planes meeting one another at definite angles does not exist.

Crystalline masses have also vectorially continuous properties (for example,optical properties), so that such masses are isotropic, but similar optical properties are common to many amorphous substances.

Lehmann first discovered plastic or flowing crystals, which have all the properties of discontinuity and homogeneity shown by ordinary crystals. He then discovered the so-called liquid crystals, which have no vectorially discontinuous properties and do not present ordinary homogeneity in their vectorial properties, although they are anisotropic; perhaps liquid crystals should more precisely be called *anisotropic liquids* or *drops* which are able transitorily to assume certain geometrical forms owing to their surface tensions (homeotropy). They are able to split and to grow like crystals, and sometimes their segmentation and budding are somewhat similar to those of living cells of microscopic plants and bacteria. For this reason they have been rashly denominated living crystals, and the attempt, as yet unjustified, has been made to attribute to liquid crystals the first origins of life.

Mlodziejowski (1913) holds that the symmetry of liquid crystals is in no way similar to that of ordinary solid crystals, so that their birefraction will not be comparable with that of true crystals. So-called liquid crystals may be drops containing traces of solid substances which cause the birefraction.

The study of liquid crystals can be very well made with silver iodide, ammonium oleate, ethyl para-azoxybenzoate, and ethyl para-azoxycinnamate.

Anisotropic drops or liquid crystals can be well observed in the case of para-azoxyphenetole and in ethyl para-azoxycinnamate dissolved in monobromonaphthalene.

EQUILIBRIUM IN HETEROGENEOUS SYSTEMS AND THE PHASE RULE

The phase rule, which was deduced and developed by the American, Willard Gibbs (1878–1889–1904), from thermodynamical considerations, explains the state of equilibrium in many physical and chemical phenomena. It was then generalised in its application by Ostwald. It may be considered, thanks to the work of Roozeboom, van't Hoff, and Bancroft, as one of the modern laws which have contributed the most to co-ordinate and explain very many chemical and physical phenomena observable in nature.

Those components of a physical system which can be separated mechanically from one another are called *phases* of that system. In homogeneous systems we have only one phase, whilst heterogeneous systems contain two or more phases. The phase of a substance, then, is any physical state, so long as it is homogeneous and well defined, in which that substance occurs. We know that the condition of a gas is determined by three variable magnitudes, temperature, pressure, and volume. For a given weight of gas we can always give two of these variables any value whatever, and the value of the third variable is then known without further determination and is dependent on the two given values.

When, for a given weight of a gas we fix any values whatever for the temperature and pressure, we know—or are able to calculate by the general gas formula, $pv = RT$—the volume corresponding with these values of the two variables. In the same way, if the values for the temperature and the volume are determined, we may calculate the value of the pressure, etc.

The density of gases diminishes as the temperature is raised and as the pressure is diminished. These two variables are called *free variables* or *degrees of freedom.*

In a gas system with a single phase we have always two degrees of freedom, that is, the system is *divariant.*

Water in a closed evacuated vessel exists in two different forms, namely, liquid water and water vapour above the liquid at a definite pressure and temperature. In this system the vapour and the liquid water are called two phases of the system. We may, however, imagine a coexistent third phase, ice, which may be formed by cooling the preceding system. The *component* of this system is always the same, namely, water in its various states of aggregation. If to the above-mentioned vessel we add an excess of salt, so that part of it remains undissolved in the water as a solid on the bottom, we shall have a system with two components, salt and water, and with three phases, namely, undissolved salt (solid phase), aqueous solution of salt (liquid phase), and water vapour (gaseous phase). If to this system an excess of another salt is then added, for example, sodium sulphate, in such quantity that a portion of this also remains undissolved, we shall have a system containing three components, sodium chloride, sodium sulphate, and water; and four phases (mechanically separable), namely, two solid phases (solid sodium chloride and solid sodium sulphate), one liquid phase (an aqueous solution of sodium chloride and sodium sulphate), and a gaseous phase formed by the water vapour.

We now see that in any heterogeneous system in equilibrium, whatever the number of the components of the solid and liquid phases of the system, there is always only one gaseous phase. Furthermore, the equilibrium between two or more phases is independent of the quantities of the individual phases present. In fact, the quantity of salt dissolved in a saturated solution (liquid phase) is independent of the quantity of undissolved salt (solid phase). In a system of several phases, when equilibrium is established, it exists both between two phases which lie side by side and between those which are separated, so that one can always eliminate any one phase without the others ceasing to be in equilibrium. A system which contains no gaseous phase, so that a liquid and a solid phase alone remain, is called a *condensed* system and the equilibrium is then almost entirely independent of the pressure, because this has a minimal influence on the volumes of solids and liquids.

The conditions of existence of a system, namely, the temperature, pressure, and concentration of the phases, are called the *variables* of the system. It is found, practically and theoretically, that the greater the number of phases resulting from a definite number of substances, the less necessary is it to know the variables in order to define the condition of a system.

In the case of a system containing a single component and three simultaneous phases, as in the case of water, noted above, with the three phases, solid (ice), liquid (water), and gas (water vapour), we know already that such a system can exist only at one definite temperature and at a definite pressure, namely, that temperature at which ice and liquid water have the same vapour pressure. This temperature is known to be 0·0075° and the vapour pressure to be 4·57 mm. of mercury, and these are sufficient data for the calculation of the concentration of the phases, that is, the other variable.

In any system with a single component, for instance, water, or in general with n components, *we have complete equilibrium when* $n + 2$ *phases are present* (that is, three phases if there is only one component). We have also seen that in this case all the variables remain fixed *a priori*, that is, there are no free variables to which we may give arbitrary values, but the equilibrium is complete and determined. If in this system we have only two phases, that is, $n + 1$, there will be incomplete but determined equilibrium, because we have one free variable to which we may give any value at pleasure, the value of the other variables being then fixed and the state of the system still sufficiently defined. For water ($n = 1$) a system with $n + 1$ phases, that is, two phases, may consist of liquid water and water vapour, or water and ice, or even ice and vapour, but in each case we have a single free variable, and, this being given, the other two are fixed in consequence. It is sufficient, in fact, to fix the value of any single variable, for instance, the temperature, because we can then deduce the other two, and all the conditions of equilibrium are thus determined. In the case of water and water vapour, for example, if we know the temperature, t, we can find the pressure of equilibrium, p, by means of a table of vapour pressures, and knowing t and p, we may easily find the concentration of the gaseous phase, that is, the number of c.c. occupied by 1 mol. of water vapour, from suitable tables. If, on the other hand, we know only the concentration of C of the gaseous phase, we can deduce p and t from the known equation (p. 65), $C = \frac{n}{v} = \frac{p}{RT}$. With all these data we can then always determine the concentration of the liquid phase if we are dealing with a substance the properties of which are well known. If, however, the temperature or the pressure in one of these systems in equilibrium is altered, equilibrium ceases, and one of the phases must disappear. In the case of liquid water and its vapour, on increasing the pressure or diminishing the temperature, the gaseous phase disappears, because the water vapour condenses; if the temperature is raised or the pressure diminished, the equilibrium is also disturbed, because the water vaporises and the liquid thus disappears. If the temperature is lowered to 0°, or below, the liquid phase is replaced by the solid phase (ice) and the gaseous phase corresponds with the vapour pressure of ice. This also will establish a definite equilibrium, because at every temperature it will have a definite vapour pressure. In the case of the ice phase, we may obtain the liquid phase at the same time by strongly increasing the pressure, because the freezing-point is thus lowered, and for any given pressure we shall have a definite temperature at which ice and liquid water can coexist. Thus the slow movement of glaciers is well explained, for when the pressure under the glacier reaches a certain magnitude, a portion of the ice is liquefied at the point of contact with the rigid surface on which the glacier rests, and the glacier moves.

In general the number of free variables or degrees of freedom can be deduced from the equation $P + L = S + 2$, where P indicates the number of phases, L the number of free variables, and S the number of substances composing the system, so that $L = S + 2 - P$.

The system of n components with n phases is determined only when two variables are fixed, and a single free variable then remains. We can, for example, have water vapour alone (one component and one phase) in various conditions of concentration, temperature, and pressure, but we can determine the state of the system at any instant if we know two variables, because the third may be easily deduced from these. In this case we have incomplete equilibrium, and the system is divariant, as we have noted above.

We may easily represent in a diagram the equilibrium of water by taking as the two axes of co-ordinates the temperature and the pressure (Fig. 36). We have already seen that the three phases of water coexist at the temperature 0·0075°, and the pressure 4·57 mm., and in the diagram this point, O, called the *triple point*, is fixed by the intersection of the three curves separating the three phases. We may in general give the name *multiple point* to that at which all phases can coexist, to which a given number of components in the system under examination can give rise.

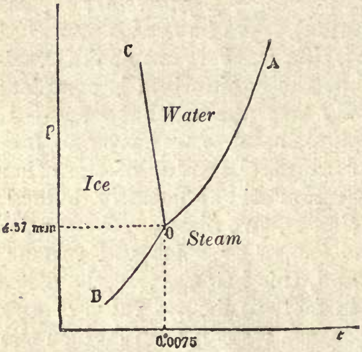


Fig. 36.

Starting from the point O, if the temperature rises the ice melts and the water remains in two phases, liquid and gaseous, which are in equilibrium only when at each given temperature we have a pressure equal to the vapour pressure. If, on the contrary, the system is exposed to a lesser pressure all the liquid will evaporate, whilst if the pressure becomes greater all the vapour will disappear and a single phase only will remain. Along the curve $O\,A$, we have points corresponding with the temperatures and vapour pressures of the liquid water representing the conditions of coexistence of these two phases. Naturally the curve cannot be continued beyond the limit A, if at this point we have the critical temperature of water, because beyond this critical temperature the liquid phase disappears, no matter what the pressure (*see* p. 29). This is to say, in a system of two phases the variability is not limitless.

Starting again from the point O, if we lower the temperature the liquid phase disappears, and ice (solid phase) is formed, although equilibrium may be maintained between the solid and the gaseous phase along the curve $O\,B$, which represents the vapour pressure of ice at various temperatures below zero, and probably tends towards absolute zero.

Returning again to the point O, if the pressure is increased the gaseous phase disappears because the vapour is condensed and ice and liquid water remain. These two phases may exist simultaneously, that is, may be in equilibrium, only at temperatures and pressures indicated by the line $O\,C$. From the direction of this line we see that the freezing-point of water is lowered with increase of pressure, and this is why ice does not liquefy with increase of pressure unless the temperature is lowered. This is a special characteristic of water, which has a greater volume in the solid than in the liquid state. For all other substances, however, the line $O\,C$ will be directed towards the right, that is to say, for them, in the solid state, no liquefaction can occur with increase of pressure; the gaseous phase is maintained in equilibrium with the solid phase if the increase of pressure corresponds with an increase of temperature, and if this latter is increased it is impossible for the gaseous phase to disappear.

In the special part of this book we shall return to this question in connection with the study of the various states of aggregation of sulphur.

We shall now study a system containing two components ($n = 2$). In the case of a saturated solution of a salt contained in a vessel together with an excess of undissolved salt, we have a system of three phases which may be separated mechanically, namely, the solid salt at the bottom of the vessel, the solution, and the vapour of the solvent which occupies the space above the solution at a given vapour pressure. The independent components are two in number: the salt and the solvent (this latter being liquid and in the state of vapour), and we have incomplete but determined equilibrium because $n + 1$ phases, that is, three phases, are present; in fact, at a certain temperature the saturated solution has a definite pressure. If under these conditions the pressure is diminished a certain quantity of the solvent is transformed into vapour, and the proportion by weight between the phases is altered, because, as the solution is saturated, a certain quantity of solid salt separates from the solution as a part of the solvent evaporates. The equilibrium between the three phases remains, however, unaltered, because if the temperature remains constant the concentration of the solution (that is, the quantity of salt per unit volume of solvent) is unchanged, and thus the vapour has the same pressure as before, because the concentration of the solution is unaltered, and there is always the same quantity of vapour in unit of volume. Equilibrium, therefore, still exists in the complex system independently of the absolute quantities of the components. When equilibrium exists, a definite temperature corresponds with each definite vapour pressure, and if at *constant* temperature the pressure is continually diminished or increased without the vapour pressure reaching the value corresponding with the fixed temperature, the solvent will continue to evaporate if the pressure continues to diminish, until only the solid substance and the vapour remain, or vapour will continue to condense until only solution and solid salt remain in the case when the pressure is continually increased.

The same phenomenon is observed if the pressure remains constant and the temperature is continuously changed.

Thus, if we have a system of $n + 1$ phases in equilibrium, we may vary the temperature or the pressure, but in the first case the pressure will remain fixed, and in the second the temperature; the system is then called *monovariant*, and the equilibrium is incomplete but determined. If in a system of two components we have two phases, then we may alter simultaneously the temperature and the concentration of one phase, by which means the third factor of the equilibrium is fixed in each case. As we have already seen, we have in this case a *divariant system* and an *incomplete and indeterminate* equilibrium. This is the case, for instance, with an unsaturated salt solution, in which there are two components, salt and water, and two phases, solution and vapour. If we diminish the pressure, part of the solvent is evaporated and the concentration of the solution increases, producing at the same time a lesser vapour pressure; a change in the system thus occurs without disappearance of either of the phases. If we continue to diminish the pressure until the saturation concentration is reached we continue to change the condition of the phases; only after this saturation point has been passed is there separation of salt, and we then have three phases, that is, we pass from an incomplete indeterminate equilibrium to an incomplete determinate equilibrium, which has already been studied above.

In a system with two components ($n = 2$) we may finally study *complete equilibrium* when there are $n + 2$ phases. Such is the case where a salt is dissolved in water to saturation without formation of a chemical compound and is present in excess and thus partially undissolved at the freezing-point of the solution. The two components are water and the salt; the phases are four (that is, $n + 2$), namely, the vapour above the solution, the saturated solution, the excess of undissolved salt, and the ice separated from the solution. In this case the ice is not formed of the solvent (water) only, as is the case for dilute solutions, but is a mixture of ice and salt, that is, a so-called *cryohydric mixture.* The temperature at which a concentrated saline solution commences to freeze is called the *cryohydric point,* and is the point at which there is complete equilibrium or coexistence of the four phases.

We may render this case clearer by studying it with the help of a diagram (Fig. 37), in which the dotted lines represent the three phases of water already studied, with the relative triple point O and curves $O\ B$, $O\ C$, $O\ A$. The freezing-point of the saturated solution of the salt (cryohydric or triple point) must necessarily be at a temperature lower than the freezing-point of water, because cryoscopic studies show (p. 88) that dissolved substances lower the freezing-point of the solvent and thus also the vapour pressure; in the diagram we find this point at O' corresponding with the temperature, t', and the vapour pressure, p', which is common to the ice and to the solution. The point O' is placed at the intersection of the curve $O\ B$ (the vapour pressure of the separated cryohydric mixture) and $O'\ A'$ (vapour pressure of the saturated solution). On raising the temperature the ice melts, and the curve $O'\ A'$ indicates the various temperatures, concentrations, and vapour pressures corresponding with saturated solutions, that is, with a triphase system.

If we increase the pressure considerably and at the same time slightly lower the temperature, the gaseous phase disappears and along the line $O'\ C'$ are found the values of temperature and pressure corresponding with the equilibrium of the triphase system—salt, saturated solution, and ice. If we alter the temperature or the pressure in such a way that the lines $O'\ C'$, $O'\ A'$, or $O'\ B'$ run to the right or to the left of the lines indicated in the figure, we then obtain a diphase system, because, if we take any point whatever on the line $O''\ A''$, corresponding with a triphase system: salt, saturated solution, and vapour (that is, in which the ice of the cryohydric mixture is absent and therefore the point O'' is at a temperature higher than O'), and lower the temperature slightly and gradually, leaving the pressure unaltered, we shall have a displacement to the left of the curve $O''\ A''$ until the gaseous phase is condensed, that is, until it disappears, and we shall obtain a corresponding dilution of the solution which, in order to become saturated again, dissolves more salt; in any case only the liquid phase and the solid phase (undissolved salt) will remain, and this modification will be comprised in the area $C''\ O''\ A''$. We may reason similarly for the displacement of other variables.

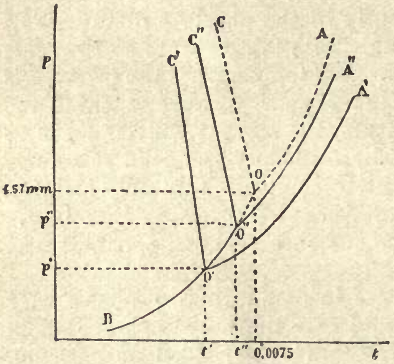


FIG. 37.

The system chlorine-water exhibits the following interesting cases: saturation of water at 0° with gaseous chlorine leads to the separation of greenish crystals of chlorine hydrate ($Cl_2 + 8H_2O$), these being stable only up to the temperature 9·6°, above which they are decomposed into gaseous chlorine and water saturated with chlorine; this hydrate is, however, stable at higher temperatures if the pressure is raised and, on the other hand, decomposes below 9° if the pressure diminishes. As a rule there are three phases for chlorine hydrate, but at a certain definite point, namely, — 0·25°, four phases are possible, *i. e.*, ice, chlorine hydrate, aqueous chlorine solution, and gaseous chlorine. The equilibrium is, however, easily altered, and at the least rise of temperature the ice disappears, whilst lowering of the temperature causes transformation of the aqueous chlorine solution into ice and chlorine hydrate and the consequent suppression of one of the four phases; this equilibrium depends also on the pressure (24·4 cm.), and if this increases, the gaseous chlorine disappears, whilst if it diminishes, another phase (the ice or the hydrate) disappears.

The phase rule is not only of considerable theoretical interest, but the result of its applications in other directions has become of the greatest importance. Thus, for example, the metallic alloys are composed entirely of mixtures of compounds formed according to the phase rule.

For this reason a certain number of determined experimental data being once known, it became possible to prepare alloys which possessed one or another desired property.

The micrographic study of metals, by means of which it became possible to analyse the state of their component phases, although it is not many years old, has led to great progress in metallurgical processes.

In another direction also all the natural igneous rocks, such as granites and gneiss, which are formed by the decomposition into phases of a fused mixture, have been studied from new scientific standpoints.

From every side, and especially in cases of complex mixtures which had not been studied until lately, except by certain empirical means and processes, the phase rule offers data of singular clearness, and explains in a marvellous manner facts which could not have been interpreted before and seemed to be due to capricious and fantastic phenomena.

RADIUM, RADIO-ACTIVITY, AND UNITY OF MATTER

We have studied above a number of laws which are obeyed by physical and chemical transformations of matter. We have seen that the most varied chemical phenomena occur without loss of weight, and thermochemical investigations have shown that in all transformations which occur in nature, the energy is maintained at a constant value with regard to quantity, only the quality varying (*see* p. 60).

Whilst the various forms of energy are capable of reciprocal transformations, in the case of matter we have found that it is impossible to transform one element into another, for example, iron into gold, etc.

If it is easy to-day to show that energy, even in its most varied transformations, can always be referred to a single form, in the case of matter such a demonstration has not yet been obtained, in spite of many experimental attempts and ingenious philosophic speculations. Until the discovery of radium nothing, or practically nothing, was known concerning the intimate nature of matter, and compared with the atomic hypothesis of the ancient Greeks practically no progress had been made in this direction. When our thought searches for the origin and intimate nature of matter with the insufficient knowledge of natural laws discovered up to our time, it is found to be impossible to obtain a rational solution of the problem of the first cause without admitting that matter itself is nothing but a form of energy.

If we are to solve this profound secret of nature without falling into the errors of metaphysics and empiricism, we must rely strictly on the known positive laws, seeking to discover new laws with the aid of experiment and of temporary rational hypotheses such as have already contributed so much to the progress of science.

We have already accepted the hypothesis of discontinuous matter, divided into many small ponderable and invisible particles called atoms, and by means of this hypothesis we have explained almost all chemical phenomena (*see* p. 22), but it is not possible to explain by this means certain important physical phenomena, especially those of the cosmic ether (*see* p. 5).

An atomic hypothesis of the nature of matter had already been propounded by William Thomson (Lord Kelvin) and by Tait, and had then been developed by Helmholtz by means of his so-called vortex atoms. According to Thomson, matter is nothing but an aggregate of vibrating nuclei formed from something which fills all space (the cosmic ether). These atomic aggregates are simply vortex movements—which differ from one another but are stable and indivisible—of various aggregates or nuclei of the ether. Such ethereal aggregates with different and perpetual vortex movements would constitute the atoms of the different chemical elements which are not transformable one into another. Tait added that these rotary movements of the various vortex atoms must be the cause of everything which affects our senses and which we call matter.

After these considerations, we shall consider somewhat further the experimental data in order to ascertain whether we can arrive at any conception of the unity of matter because, the unity of energy having been demonstrated experimentally, it appears strange that the matter present in nature should always be subdivided into seventy-five or eighty different kinds (elements), whilst all the other sciences, including zoology and botany, tend to show the convergence of the most various organisms towards ever simpler organisms, until they arrive at a single primary cell. All this tends towards monism.

After the work of Dalton and his ingenious atomic hypothesis, and after that of Lavoisier, Gay-Lussac, Proust, Berthollet, Richter, etc., at the end of the eighteenth century and the beginning of the nineteenth, after many of the atomic weights had been determined, and after the lightest substance, hydrogen, had been chosen as the element of comparison, W. Prout, a London medical man, started in 1815 a somewhat hazardous hypothesis on the unity of matter. Assuming that the atomic weights of the elements were exact multiples of the atomic weight of hydrogen, he concluded that the atoms of all the chemical elements were nothing but stable aggregates of various numbers of hydrogen atoms; thus hydrogen would be the single primary material from which all the other elements were derived. Meinecke (in Germany) in 1818 and Thomson (in England) supported this hypothesis strenuously, together with a few other chemists, whilst Berzelius, who was at that time much occupied with the study of atomic and molecular weights, combated it, showing that the integral atomic weights chosen by W. Prout and by Thomson were not deduced from experimental determinations, but had been considerably modified; this was confirmed by Turner in 1829. On the other hand, the supporters of Prout's hypothesis replied that the small fractions in the values of the atomic weights were the result of inevitable experimental errors. Pointing then to the discovery, just before that time, of the free alkali metals by Davy—who separated them electrolytically from the alkalis, which had up to that time been held to be simple bodies—many chemists supported Prout's hypothesis as the most plausible and as that which justified the hope of decomposing many other substances supposed to be simple. Under the influence of Berzelius, Prout's hypothesis was, however, universally rejected, and was only taken up again with much ardour by the eminent scientists Dumas and Stas when they found that the atomic weight of carbon was exactly equal to 12, whereas Berzelius had confidently given to it a higher fractional number.

Dumas and Stas then set themselves to control many atomic weights by means of an extraordinary wealth of experiments and of scientific apparatus, with a view to confirming Prout's hypothesis. After a prodigious amount of very accurate work occupying several years, during which Dumas was able to control rigorously the atomic weights of more than twenty elements, the two scientists came to diametrically opposite conclusions. In 1858 Dumas declared himself a partisan of Prout's hypothesis, while Stas declared the contrary, thus causing a division of opinion between certain chemists. Marignac in Geneva also contributed to the dispute by means of very valuable work, and in order to support the hypothesis of Prout he supposed that the atomic weight of an element was not constant, but oscillated about the nearest whole number. Landolt was, however, able to demonstrate by means of exact determinations that chemical combinations occur in a manner rigorously fixed with regard to weight, and that certain atomic weights are known with an accuracy which extends to three decimal places.

However, when Ostwald recently succeeded in establishing oxygen, with the atomic weight of 16, as the standard for the other elements, with the approval of the majority of chemists, many of the atomic weights of the latter which were found to be represented by fractional numbers when referred to hydrogen, became whole numbers. Some of the difficulties concerning the hypothesis of the unity of matter thus disappeared if the existence of some primary element, two or four times lighter than hydrogen, were admitted. To-day, however, if a primary and single form of matter is spoken of it is necessary to think of atoms immensely smaller than those of hydrogen, such as we have vaguely noticed in the study of ions and of electrons. In fact the differences of weight found by Landolt and Heydweiller during chemical combination (*see* Note on p. 9) are of an order of magnitude so small that we may perhaps explain them with the help of recent views on the size of electrons, and in harmony with important phenomena of radioactive bodies, and we may perhaps confirm the conception of Marignac, whose determinations of atomic weights do not lead to constant weights, but to values oscillating about certain whole numbers.

Many other facts attract our thought towards the seductive hypothesis of the unity of matter, and we must note the periodicity in the chemical and physical properties of the elements which was brilliantly shown by Mendelejew by means of his periodic system of the elements (*see* end of this volume). Certain physical and chemical properties are, in fact, a true function of the atomic weights. The elements of certain groups, taken in the order of their chemical atomic weights, show a regular and gradual modification of physical and chemical properties.

In the allotropic forms of certain elements, for example, of oxygen (which also forms ozone), we have two substances with different chemical and physical properties although formed of a single elementary material, oxygen, this difference being explained by the different numbers of similar atoms which enter into the molecules. We have still more important examples in the numerous isomerides and stereoisomerides of organic compounds, which differ from one another physically and chemically, although they are constituted of the same elements (for example, fumaric and maleic acids, $C_4H_4O_4$), and which are, moreover, transformed into one another with the greatest ease. These facts being known, it does not appear to be heresy to suppose that the atoms of various elements may be composed in their turn of still smaller particles of the same nature, only the number and arrangement of these showing variations.

If we consider also the ionic hypothesis of Arrhenius, we see that the molecules and atoms of the free elements have chemical and physical properties very different from those of the corresponding ions. The relations—first discovered by Ciamician and later by Grünwald, and especially by Kayser—between the spectroscopic constants of the elements and their atomic weights showed once more how certain physical and chemical properties are functions of the atomic weights.

The important observations of Lockyer on the spectra of heavenly bodies led to the belief in a gradual decomposition of the elements themselves, when these are exposed to very high temperatures. Crookes, in his important work on the rare earths of cerite, enunciated the hypothesis of the evolution of the atoms, referring them all to a primordial material which he called *protyl*.

Such were the knowledge and hypotheses current until a few years ago, when a sensational discovery illuminated this field of uncertainty. This was the discovery of RADIUM, which removed the problem from the realm of hypothesis to that of positive experimental facts, which showed that beyond the atom there existed a further marvellous world, and furnished a rigorous proof that the hope of the alchemists of the transformation of one atom into another was not altogether a dream.

At this point we may give a brief account of radium and radio-activity.

For many years the phenomena of fluorescence and phosphorescence have been well known. A fluorescent substance becomes luminous when exposed to the action of the ultraviolet rays of the spectrum which are not perceptible to our eyes on account of the very great frequency of their vibrations (*see* p. 6); such a substance lowers the frequency of the ultra-violet radiations so that they are rendered visible, but the luminosity only lasts while the substance is actually exposed to these dark rays. Many phosphorescent substances, on the other hand, become luminous after being subjected to the action of daylight and remain luminous even after the action of the light has ceased, that is, in total darkness. All substances appear to be capable of phosphorescence, but in some cases the phosphorescence lasts only for a single instant (a few thousandths of a second), whilst in other cases it lasts for hours or even weeks. Phosphorescence may also be provoked by percussion, friction, the action of thermal and electrical vibrations, etc.[1] Very interesting substances have now been discovered which are able to emit light and heat continuously, even without the action of any stimulating agent; these are the radio-active substances which have been studied during the last few years.

In 1896 Becquerel discovered that uraninite or pitch-blende, without having been rendered phosphorescent by exposure to daylight, emits special radiations capable of influencing a photographic plate, radiations which are propagated in straight lines, but cannot be reflected, refracted, or polarised. These rays render gases good conductors of electricity and discharge an electroscope even at a distance, that is, they convert so-called

---

[1] Many of these phenomena are to-day comprised under the generic term of luminescence. Any body which is at a temperature above — 273° emits and exchanges energy with its surroundings. Our eye perceives as true luminous energy only that due to calorific radiations emitted by bodies when they are heated to at least 360°. All the other forms of luminosity, even at low temperatures, are comprised in the term *luminescence*, which accompanies many chemical phenomena. Its intensity increases with the thermal tonality and with the velocity of reaction, which, however, has no influence on its colour. The theory of luminescence has not yet been evolved, although it is closely related to the theory of electrons and of dispersion.

insulating substances into conductors of electricity. Becquerel attributed these properties to uranium and uranium compounds, but in 1898 and 1899 Madame Sklodowska Curie and her husband, Professor Curie, showed that these special properties were much more marked in certain pitch-blende residues from which the greater part of the uranium had been extracted. They concluded, therefore, that the cause of these phenomena must be attributed to another substance, which they called polonium, and which they hoped to be able to isolate from large quantities of these residues.

They were, however, soon able to separate a substance a million times more active than uranium, and to this they gave the name of radium. In 1899 Debierne believed that he had isolated another active substance, to which he gave the name of actinium. To-day we can safely affirm the existence only of radium in the various compounds which have been studied. From the last researches of Curie (1910) the existence of polonium also appears to be confirmed. In 1902 Rutherford, on the other hand, had separated from thorium preparations, imponderable quantities of a radio-active substance called thorium X (radio-thorium); he found that this continued to be formed from elementary thorium, but that it developed an emanation and gradually lost its radio-activity. Rutherford concluded from these facts that the material atoms of radio-active substances are in a state of continuous transformation, and thus arrived at the first theory of radio-active substances.

Radium is an element which is chemically very similar to barium. From the pure bromide, $RaBr_2, 2H_2O$, the atomic weight of radium was found to be 225, now corrected to 226·4. Radium compounds have a smell of ozone because they form this from the oxygen of the air. They continuously emit heat and a very small quantity of a peculiar light. They have an irritating action on the epidermis and, if prolonged, the contact ends in the production of blisters. Radium is found only in minimal quantities in nature, but is widely diffused. In order to obtain twenty centigrams of radium bromide, Madame Curie worked up two tons of pitch-blende.

In 1903 Ramsay and Soddy, on studying radium spectroscopically, made the surprising observation that of eight principal lines four or five are at first common to the helium spectrum, but that the spectrum then alters and the radium continues to be transformed into another substance not yet defined, from which, as a final product, helium, which is readily visible in the spectrum, is formed. This interesting phenomenon was confirmed later by Debierne, Giesel, Curie, Dewar, Himstedt, G. Meyer, and others, and the supposition of Lord Kelvin that the helium might have been occluded in the radio-active substance was excluded. Actinium also produces helium, and in general all the radio-active substances produce α-rays, formed of α-particles, the atomic weight of which is identical with that of helium, so that this latter must be formed of α-particles deprived of the electric charge; the α-rays decompose water even at $-180°$. One gram of radium produces 144 to 219 cu. mm. of helium per annum and would require tens of thousands of years to be transformed completely into helium. Radium had scarcely been discovered when some objected that its inexhaustible activity (which does not diminish) was in contradiction to the fundamental law of the conservation of energy (*see* p. 4). Now, however, it is clear that a diminution of energy, namely, transformation into helium, does take place, but that it is so small that it escapes all ordinary measurements, and tests extending over years would be necessary in order to determine it. All the properties of radium remain unaltered even at 180° below zero, although at $-150°$ the radium emanation condenses and then shows no vapour pressure. In fact, when a current of air is passed over radium at that temperature, the emanation does not pass into the air. Further, the emanation of a radium salt is almost zero in a perfectly evacuated tube. Ramsay and Gray in 1909 liquefied and even solidified the emanation at very low temperatures. In 1906 Battelli succeeded in condensing the emanation by cooling with liquid air the gas from the waters of the S. Giuliano baths, this rendering luminescent tubes smeared with zinc sulphide.

The liquid emanation has a specific gravity of 6·8, boils at $-62°$, has a critical temperature of 104·5°, a critical pressure of 47·45 mm., and an atomic weight of 222·4; it melts at $-71°$; it rapidly undergoes change to about half of its weight (in four days). The liquid emanation is transparent and colourless like water and phosphoresces with various colours according to the quality of the glass of the containing vessel. When solid it is opaque, but gives a steel-blue phosphorescence. When cooled further it assumes a yellow colour, and at the temperature of liquid air it shows a shining orange-red colour. Ramsay has given the name *niton* to this emanation. The whole behaviour of radium was from the beginning an enigma, for the exact scientific interpretation of which there were not wanting hardened devotees of dogma and metaphysics who attempted to proclaim that science was again bankrupt.

To-day, however, these phenomena have all re-entered the orbit of general and fundamental laws, thus advantageously enlarging our scientific horizon. We shall now give a simple interpretation of these apparently strange phenomena.

If an almost absolute vacuum (as low as a few millionths of an atmosphere) is maintained in a glass tube containing electrodes united to an induction coil, when an electric discharge is passed rays are projected from the cathode in a direction normal to its surface, independently of the position occupied by the anode. These cathodic rays, also called β-rays, have the power of heating bodies which they irradiate and of rendering them luminous, producing an emanation of X-rays (Röntgen rays or γ-rays). They are able to traverse thin aluminium plates, and cause gases and all bodies through which they are propagated to become good conductors of electricity. It has also been found that these rays are diverted from their rectilinear course under the action of a magnet and behave as though they were constituted of negatively charged material particles. On studying the relation between the electric charge and the mass of these moving particles (Electrons, p. 105), it is found that this ratio is about two thousand times greater than that of the hydrogen ion compared with its charge, 1·008 grms. of hydrogen having a charge of 96,540 coulombs (p. 94). Consequently, if the moving particles of the cathodic rays have a mass equal to that of the ions, they must have a charge two thousand times as great, or if the electric charges are equal to those of the ions, then the mass of these particles must be two thousand times smaller, which is also very probable from considerations of quite another order. The negative rays would hence be constituted of free negative electrons moving with a velocity of 60,000 kilometres per second, and we can thus understand why bodies which receive these particles undergo a kind of bombardment and become heated. The γ-rays are electrically neutral, as they are not diverted by a magnet, but they are endowed with a very great power of penetration into opaque bodies, and, according to Tuomikoski (1909), are able to traverse a block of lead of a thickness of 19 cms. They have vibratory properties similar to those attributed to the cosmic ether.[1]

Positive electrons are also known which form the anodic rays or α-rays, Goldstein's rays or canal-rays, which pass from the anode in the evacuated tube mentioned above, and proceed to the cathode, by which they are absorbed, as they have not the property of passing through metals; if there is a small hole in the cathode which permits them to pass, they continue their course along a glass tube fixed to the hole behind the anode. On studying these rays it is found that they do not traverse an aluminium plate, and that they are diverted by a magnet in the opposite direction to the cathode rays. They are also repelled by positively charged bodies, so that they are considered to be formed of positively charged particles (electrons), which have a velocity of about 1000 kilometres per second, whilst negative electrons may with certainty be described as units or free atoms of electrical energy (J. J. Thomson), and hence may be regarded as a new substance (Ramsay, 1908). The existence of free positive electrons has not yet been proved, and as these are always united to particles of matter, we have not been able to demonstrate experimentally that they also are formed of an agglomeration of atoms of energy. If this were so, then all matter would be formed simply of various aggregates of positive and negative energy. Ramsay hence believes that until we are able to liberate positive electrons these must be considered as *matter* itself or as the essence of matter, whilst energy is represented by negative electrons.

The relation between the electric charge and the mass of the positive electrons is almost equal to that between the electric charge of the ions and their mass. Thus, the mass of the positive electrons is about two thousand times as great as that of the negative electrons and corresponds with the mass of the ions. As mentioned above, Rutherford showed experimentally that the particles of the α-rays are identical with the atom of helium, and this had, moreover, been theoretically predicted by him before Ramsay discovered the formation of helium from radium; the α-particles should have a weight double that of the hydrogen molecule, that is, a weight equal to that of the atom of helium (4).

Experiment has shown that the electrons of opposite signs have different masses and

---

[1] The action of X-rays has sometimes dire effects, and Dr. Wilson, who made many radiographic investigations at the London Hospital, had to undergo two surgical operations in 1906, two in 1908, and two again in 1910, while in March 1911 he succumbed, although still a young man.

velocities, and for various reasons we may also suppose that the material atoms of various substances are merely aggregates of positive electrons, of which the electric charge is due to the negative electrons. After these considerations, the nature of radium is rendered less obscure, as it has been shown that this emits few X-rays and α-rays, whilst it continually emits many β-rays formed of negative electrons which have the interesting properties already studied. We also understand, then, why radium does not apparently diminish in weight, because the electrons which are projected consist of such extremely small quantities of matter that we should not be able to appreciate on our most delicate balances the loss which would occur even through a period of many years. These particles are, however, charged with such large quantities of energy and are endowed with such a velocity that on colliding with surrounding bodies they cause an elevation of temperature. The radiations, and especially the β-rays, produce ozone from the air, and slowly decompose water vapour with formation of hydrogen, hydrogen peroxide, and oxygen, whilst the γ-rays do not show any such phenomena.

The ionisation of gases would consist in the dissociation of molecules or in the separation of a negative electron from an atom, which thus becomes a positive ion, whilst the negative electron liberated may unite with an atom, transforming the latter into a negative ion. Ionisation of gases may be effected either by means of radio-active substances or by the action of ultra-violet rays, cathode rays, or X-rays, or by heating to incandescence.[1]

---

[1] **USES, PREPARATION, AND INDUSTRY OF RADIUM.** Many varied and often fanciful applications have been proposed for radium, but only a few have been found of real importance : mention may be made of the extraordinary cures of lupus, the encouraging results in the treatment of cancer, the removal of epithelial tumours, of ulcers and chronic pruritus of the skin. Industrially it is used to measure the electrical energy of conductors, to prevent fabrics and machines from being electrified—silk fabrics, for instance, being passed directly into baths containing radium. The latter is also thought to be of agricultural value, on account of its fertilising and anti-parasitic actions; seeds steeped in radio-active water certainly germinate the more readily. Gudzent has shown that respiration of the emanation of radium D does away with the deposits and with the absorption of uric acid.

In medicine use is generally made of the γ-radiations (which are endowed with a velocity equal to that of light and have the maximum penetrating power). The β-rays, which are less penetrating, and the α-rays, less penetrating still (although they move at a speed twenty times that of light), are separated from the γ-rays by passing the mixture of the three through screens of suitable thickness. The use of radium emanation in cases of anæmia and tuberculosis has also been suggested, but as the emanation does not traverse solid bodies, the radium salt must be administered by ingestion or injection and is thus lost; in some animals, however, the blood remains radio-active for some months after injection of insoluble radium salts.

For external cures radio-active pastes or varnishes are prepared and applied to the parts affected; no anæsthetic is then required and no pain is caused. The radium salt is enclosed in a platinum tube rather more than 2 cm. in length, this being placed in a leather sheath; the latter acts as a filter and retains the α- and β-rays, which are the more destructive to normal tissues, but allows the γ-rays to pass. The tube, held by some plastic material, is placed close to the diseased part of the body, in which incisions are sometimes made. The action of radium on cancerous tissues begins immediately, the application lasting 4 to 24 hours. In some instances the tumour disappears after a month or six weeks.

A slight idea of the enormous amount of work required to separate radium from various minerals is given by the following summary of the process suggested by S. Radcliff (1914) for working up the somewhat poor ores of Olary : The material is first ground, sieved, and subjected to concentration (enrichment) by means of magnets. Each 500 kilos of the enriched product is fused for 8 hours with 1500 kilos of sodium bisulphate, the mass being then allowed to solidify, broken up, powdered, sieved, thoroughly washed with water, and allowed to settle. The clear solution containing the uranium is decanted from the sludge and heated with sodium carbonate or bicarbonate to remove the iron and other bases, the solution being afterwards acidified and the elimination of the carbon dioxide completed by means of a current of air. The uranium is then precipitated by ammonia, and the whole concentrated, dried in a muffle and well washed, the final product containing 75 per cent. of U_3O_8. The sludge mentioned above is concentrated, left for some days in contact with one-half its weight of sulphuric acid, and filtered, the residue on the filter being washed, boiled for two days with 20 per cent. sodium carbonate solution to convert the sulphates into carbonates, and again thoroughly washed. The remaining sludge is digested with hot dilute hydrochloric acid and allowed to settle, the clear liquid being decanted off and the lead, barium, and radium in it precipitated as sulphates by addition of sulphuric acid; the residue is digested a second time with hydrochloric acid. The crude radium sulphate is next either treated according to the Soddy process to recover the radium or subjected to the action of a stream of hydrogen chloride to precipitate the chlorides, those richest in radium being thrown out first. The sulphates may also be reduced by means of calcium hydride.

The purest radium preparations sold consist of a mixture of much barium chloride with traces of radium chloride and cost 20 to 24 shillings per gram. A mixture of barium bromide and radium bromide containing 10 per cent. of the latter costs £40 per gram, while the price of radium bromide

In harmony with these considerations, we may suppose matter to be constituted of particles much smaller than the chemical atom which is found free in ordinary chemical reactions: particles carrying large electric charges and grouped in varying numbers in more complex and more stable systems, which perhaps constitute the atoms of the various chemical elements. We shall then understand the slow and gradual transformation of radium into helium, which would be merely an orientation and regrouping of the electrons of radium into a more stable system, that of helium; that is to say, radium is an element in a state of coming into existence. The radio-activity would then be due to the continuous liberation of negative electrons from the material nucleus of radium, in which the larger positive electrons would remain in preponderance, while the negative electrons rotated round them. This hypothesis furnishes also the simplest and most logical interpretation of the unity of matter, as the atoms of the common elements may be considered as formed by the grouping of various numbers of these electrons, which at the instant of their union lose their powerful electric charges in the form of light and heat. According to Rutherford, these emanations of electrons cause a species of explosion of the complex atoms of radio-active substances, so that a few elementary particles are set free and are projected with an extraordinary velocity (electrons), whilst the remaining particles collect into more and more stable systems until they gradually become atoms of the common elements known to us, for example, helium. Thus radium is transformed first into a gaseous emanation, which then becomes solid at the ordinary temperature, forming radium *A*, this gradually giving origin to radium *B*, *C*, and *D*, and finally radium *F*. When these substances are deposited, even in minimal traces, on other bodies, the latter become radio-active. Radium *F* would be the polonium of Madame Curie. Radium is, in turn, the fourth term in the slow transformation of uranium (occupying thousands of years), which has for its first term uranium *X*, then ionium, radium, emanation, radium *A*, etc. From actinium would be derived the other series, radio-actinium, actinium *X*, emanation, actinium *A*, *B*, and *C*; the third series of radio-active substances would be formed by thorium, mesothorium 1, mesothorium 2, radiothorium, emanation, thorium *A*, *B*, and *C*. The γ-rays are specially produced by radium *C*, and can be separated from the α- and β-rays by passing them through lead plates, which allow only the γ-rays to pass. All these new radio-active elements are not yet sufficiently studied, and up to the present are distinguished from one another by the various kinds of radiation (α, β, γ), by the velocity of these, which is measurable by their power of penetration of an aluminium plate, or by their ionising powers in air. They are also distinguished by the rapidity of transformation of one term of the series into the next, a rapidity which is measured by the diminution of their radio-activity; actinium emanation, for example, is already transformed to half its extent in four seconds, whilst uranium requires six thousand million years.

This new family of radio-active substances, now embracing more than thirty elements, has found its proper position in the periodic system of the elements (see last chapter of this volume) as a result of the work of Fajans (1913). The series of elements which emit

---

itself was £400 per gram in 1909 and more than £1200 per gram in 1913. In 1909 the Austrian Government sold by auction the first gram of pure radium salt prepared by Joachimsthal (where the pitch-blende contains as much as 45 per cent. of uranium), and there were several bidders at £16,000 per gram. An International Commission, with Rutherford as president, met at Paris in March 1912 to fix standards for radium preparations, and in 1913 seven, destined for different countries, were prepared by the Radium Institute of Vienna. The standard prepared for England was analysed, St. Meyer at Vienna finding it to contain 21·10 mgrms. of radium chloride ($RaCl_2$) and Mme. Curie at Paris, 21·16 mgrms. Radium preparations are kept in glass vessels surrounded by very thick lead coatings; the emanations are also retained by six layers of silk heavily weighted with lead and tin phosphates.

In the United States radium has been extracted since 1903 from carnotite (uranium vanadate), which abounds in various regions, especially in Colorado (Paradox district). The cost of extracting, sieving, and bagging the mineral amounts to £6 to £8 per ton, freight to Placerville about £4 and thence to Hamburg about £2 16*s*. per ton. The sale price of the mineral is based on the content of uranium and increases more rapidly than this; in 1914, mineral containing 2 per cent. of uranium cost about 21*s*. per kilo of uranium oxide present, with a premium of about 13*d*. per kilo of vanadium. In 1913, 2140 tons of dry carnotite were extracted at Newmire in San Miguel County (Colorado), this corresponding with 38 tons of uranium oxide (26 tons in 1912) and 914 tons of vanadium oxide. Three thousand kilos of uranium correspond with about 1 gram of radium, not all extractable, so that the above production would be equivalent to about 9 grams of radium chloride. The Austrian production of radium chloride in 1911 was 2·647 grams, and that of the rest of the world 1·5 grams of radium chloride.

α-particles are found in a group retarded by two positions and those emitting β-particles in a group advanced by one position, so that uranium *I* belongs to Group VI; uranium X_1, which is derived from *I* by emanation of α-particles, will belong to Group IV, and uranium X_2, derived from X_1 by emanation of β-particles, to Group V; uranium *II*, derived from X_2 by emanation of β-particles, belongs to Group VI. Ionium, formed from uranium *II* by emanation of α-particles, belongs to Group IV, and radium, derived from ionium by emanation of α-particles, to Group II, while the emanation derived from radium by α-radiations belongs to Group O or VIII, these being identical; radium *A*, derived from the emanation by α-radiation, belongs to Group VI. That this classification is justified is shown by the fact that the α-particles carry two elementary charges of positive electricity, whilst the β-particles carry one elementary charge of negative electricity. Since the α-particles are atoms of helium with the atomic weight 4, the atomic weights of elements which emit α-particles will diminish by 4; β-particles, on the other hand, are electrons with an extremely small weight compared with that of the atoms, so that elements emitting β-particles do not change in atomic weight. The values for the radium-uranium series are: uranium *I*, 238·5; uranium X_1, 234·5; uranium X_2, 234·5; uranium *II*, 234·5; ionium, 230·5; radium, 226·5; emanation, 222·5; radium *A*, 218·5. Such of these substances as belong to the same group are not distinguishable chemically, even when their atomic weights are different, and this is now understood from their position in the periodic system of the elements; this is the case with radium and mesothorium *I*, both belonging to Group II. The elements of the final transformation in the three series, namely, radium, thorium, and actinium, fall into the same group in which lead occurs, and are hence identical with the latter, although of different atomic weights; thus lead may be regarded as consisting of different elements with slightly different atomic weights but of identical properties, and it would not be surprising if emanation of α-particles from thallium yielded an atom having the same properties as gold, although of different atomic weight. Those elements with identical properties but different atomic weights form pleiads, which belong to one and the same group of the periodic system.

Ramsay recently suggested (in 1908) that the difference between the various elements depends on the loss or addition of electrons, and that the transmutation of the elements is thus possible; he declared further that he had transformed copper into lithium by the action of radium emanation (a fact seriously contested by Madame Curie and by Gleditsch), that he had obtained carbon monoxide and dioxide by acting with radium emanation on the following group of elements: silicon, titanium, zirconium, thorium, and lead, and that the action of niton (the emanation of radium) on water yields neon. In 1909, Rutherford and Royds showed that the α-particles of radio-active substances are none other than helium atoms carrying an electric charge, and in the same year Perman showed that copper and gold do not undergo any change through the action of radium bromide. The statements of Ramsay, therefore, need to be confirmed by other experimentalists before they can be accepted as decisive. J. J. Thomson considers that the elements of Ramsay's transformation pre-existed in the electrodes, to which they were so adherent that they were not detached by heat, and that they were liberated by the electronic bombardment of the electrodes. To detect minimal traces of these gases, Thomson used a method more sensitive even than the spectroscopic method; he subjected a small bundle of positive rays (canal rays) to the action of a powerful magnetic field and determined photographically the extent of the deviation, this indicating the mass, *i. e.*, the atomic weight of the particles, since the deviation of a single particle depends on the ratio between its charge and the mass (*see* p. 127). The formation of radium from uranium appears to have been demonstrated experimentally with certainty by Soddy in 1909; thus a solution of pure uranyl nitrate which did not contain any radium certainly contained radium after three years had elapsed.

The chemical atoms constituting our simple substances should, therefore, be very stable systems, because it has not been found possible by any method to restore to them the energy which they have lost in order to transform them into electrons. By means of these conceptions we are already better able to explain why our immense source of light and heat, the sun, has not yet been exhausted. The chemical reactions which occur incessantly in the sun and the condensation of matter would not suffice to compensate for the heat lost through continual thermal radiation, and the sun would to-day be cooled much more perceptibly if there were not some continuous and powerful source of potential energy which is incessantly transformed into actual energy (*see* p. 6). The solar mass is perhaps still constituted in part of free electrons, which are gradually being converted into various elements, thus developing such an amount of heat as almost compensates that lost by the sun. As a matter of fact helium and uranium abound in the solar photosphere, and this fact increases the probability of this hypothesis.[1]

In conclusion, although we admit that all these facts tend towards the hypothesis of the unity of matter, or better, of the existence of energy only, up to the present the experimental results in this field are not sufficiently advanced for us to accept this hypothesis as definitely proved. Of all the elements, we have seen that only radium is transformed into helium, but not iron into gold, hydrogen into copper, or any of the better known elements into any other. If there is any tendency, it is in the sense of a transformation of an element of high atomic weight into one of lower atomic weight; thus Ramsay affirmed that he obtained traces of lithium by the action of the radium emanation on copper. He also decomposed hydrochloric acid, ammonia, and carbon dioxide into their elements, and finally regenerated these compounds from their respective elements by means of radium emanation (1908).

But the close veil which hid these important secrets of nature has been rent. Science and progress will remove it completely in the near future.[2]

---

[1] In 1914 A. Verronet submitted to re-examination the most reasonable explanations of the solar heat. Although he did not exclude the hypothesis that the heat is derived from chemical reactions or is due to the formation of the elements from electrons with liberation of thermal energy, he regards as the most probable Helmholtz's hypothesis, which is based on calculation of the heat produced by the gradual and continuous contraction of the solar mass. Helmholtz calculated that the total contraction (solidification and cooling) of the sun would produce a quantity of work equivalent to 20,000,000 times the heat annually radiated from the sun. From the diminution of solar radiation owing to gradual fall of temperature, it is calculated that this radiation has been proceeding for about 2,000,000 years and that after the lapse of a further equal period the temperature of the earth will not fall to 0°, account being taken of the fact that the earth is slowly approaching the sun. According to geologists, the age of the earth is about 100,000,000 years, if erosion took place in the past at the same rate as at present. Since, however, the temperature was higher, evaporation from the sea more rapid, and rain more frequent and abundant, erosion in the past must have been, on an average, ten times as intense and fast as nowadays, so that the geological age of the earth must be reduced at least to 10,000,000 years.

Perry (1912) explains part of the solar heat as due to the continuous increase of the mass of the sun by the numerous meteorites falling into it with enormous velocities. H. S. Shelton (1913) points out that, according to this hypothesis, many of such meteorites should have encountered the earth and left traces in our sedimentary rocks; no traces are, however, found, and even at the present time only very small and very rare meteorites strike the earth. Shelton also regards the radium theory as inadequate to explain solar heat, since radium is a transitory element with a life, under normal conditions, far shorter than the geological era, which he considers the most trustworthy (*see above*). Further, this author does not think the explanation lies in uranium (which generates radium), which has a life enormously longer than radium, since the spectroscope shows that uranium is not very abundant in the sun. Shelton regards as more reliable the hypothesis of the transmutation of the elements, this view being based on the spectral lines indicating the stage reached by any given star. First come gaseous nebulæ with spectra exhibiting few bright lines and revealing the presence of hydrogen, helium, and some unknown substances; this is the first stage of stellar evolution. In the second place are stars of the helium type, containing certain metals in addition to hydrogen and helium, and in the third, stars of the hydrogen type, showing a greater complexity of composition.

From the hydrogen type insensible gradations lead to stars of solar type, of still more complicated composition, their spectra showing clearly the lines of iron and other heavy metals. Finally, come the dark red stars showing spectra containing a large number of lines and exhibiting signs of cooling and decadence.

Elements which are stable under conditions realisable in the laboratory undergo—at the very high temperatures of the stars—changes, and gradually assume more stable forms, with evolution of enormous quantities of thermal energy.

[2] To the deductions which have just been arrived at we may also add the following new considerations. Since the nature of the electrons is itself independent of the composition of the electrodes, and of that of the gas which fills the space where these electrons are produced, and as also the same kind of electron is always produced when any gas is exposed to the action of Röntgen rays or when a metallic plate is irradiated with ultra-violet rays, it may be argued that all matter is constituted of a single principle, the electron.

H. A. Lorentz, with his electro-magnetic theory of light, according to which the electro-magnetic undulations which produce luminous impressions on our eye are the product of the movement of material particles one thousand times smaller than the atom of hydrogen and carrying a negative electric charge, would support this hypothesis. Furthermore, we may mention the interesting experiments of Zeemann, who succeeded in influencing the spectroscopic character of light emitted from incandescent substances, by the action of powerful magnetic forces.

A. Debierne has also succeeded in transforming actinium into helium. It has also been shown that the radium which exists to-day represents half the weight of that which was present ten

We shall therefore still continue to refer phenomena to the molecules, atoms, and ions of various substances as we have assumed them in the study of the laws which govern matter in its various manifestations; the basis of these general laws having been explained, we shall now undertake the systematic study of the various elements and of their more important compounds.

---

thousand years ago, at which epoch it was probably formed, and probably in a further ten thousand years almost all the radium existing will have been transformed. During this geological epoch our terra-aqueous globe has not undergone such profound changes as to justify the appearance *de novo* of a new element on the earth, and thus the hypothesis becomes plausible that radium itself is formed by the slow and intimate decomposition of another element of higher atomic weight. We know only two elements of atomic weight higher than that of radium, namely, thorium and uranium. As a matter of fact, uranium minerals always contain radium, and Soddy succeeded in showing the continuous formation of radium from uranium nitrate even after all traces of radium had been carefully removed. If the disintegration of radium during its transformation into helium lasts ten thousand years, the disintegration of uranium is estimated at ten million years.

Whilst the heat liberated during the formation of a molecule of various substances may rise to a maximum of one hundred thousand calories, that liberated by a corresponding quantity of radio-active matter in its evolution into substances of more stable character is calculated at thousands of millions of calories.

II. SPECIAL PART

CLASSIFICATION OF THE ELEMENTS

The division of the elements into two classes, non-metals and metals, is somewhat arbitrary. However, we retain this classification, partly because a certain characteristic difference exists between these two groups, partly for didactic convenience, and also because it is usual.

The metals, when polished, have a characteristic lustrous appearance, and are all solid, excepting mercury; the *non-metals* have rarely this appearance, and are never malleable and ductile like the metals; some of them are gaseous.

The metals are good conductors of heat and electricity, and their conductivity decreases as the temperature is raised; the *non-metals*, on the contrary, are less good conductors of heat and electricity, and their conductivity decreases as the temperature is lowered.

The metals rarely combine with hydrogen, and then form solid compounds; on the other hand, *non-metals* usually combine with hydrogen to form gaseous compounds.

The metals unite with oxygen to form compounds which, when dissolved in water, have a more or less basic character, the reaction being alkaline or, occasionally, weakly acid; *non-metals*, on the other hand, combine with oxygen to form compounds which dissolve in water to form liquids of markedly acid character.

On decomposing by the electric current a substance containing metals and non-metals, the latter migrate to the positive pole and the metals to the negative pole. In Part III of this treatise the general properties and characteristics of the metals are summarised.

The metals and non-metals are further subdivided into various groups in which those elements are collected which have the same valency and a progressive analogy in their physical and chemical properties, and in the composition and behaviour of the compounds which they form. This more or less complete relation between elements of the same group and their derivatives was made evident by the ingenious classification made by Mendeléev in 1859, in his periodic system of the elements, which will be best understood when the properties of the elements and of their compounds have been studied; it will therefore be considered at the end of the book.

Hydrogen cannot be included in any of these groups, and in many of its properties it is related rather to the metals, although a gas. For this reason we shall discuss it alone and before the other elements.

HYDROGEN : H, 1.008

This element was first obtained, under the name of inflammable air, by treating iron with a dilute acid. It is a gas which is found free in very small quantities on the earth. Bunsen in 1852 and others later (St. Claire Deville, Leblanc, Fouqué) have found it in volcanic exhalations and lava, where it is perhaps produced by the action of steam on metallic nitrides and hydrides. It has also been found in the gaseous inclusions of some Stassfurt minerals (Reichardt, 1860); in granite, gabbro, and basalt (mixed with 10 per cent. of methane), from which it is obtained by heating the powdered mineral to redness; strongly compressed in some meteorites (*e. g.*, that of Lenardo and another from South Carolina, 1886), which contain also argon and helium; in the inflammable gas which is evolved in certain countries, and in petroleum springs. Free hydrogen is abundantly present in the solar photosphere, in other stars, and in all nebulæ of which the light has been analysed by the spectroscope. It is formed amongst the gases evolved during certain fermentations—especially that of cellulose—caused by anaerobic micro-organisms, and is thus also found in coal, in peat, and in the intestines of certain animals, especially cattle, during the fermentation or putrefaction of their food, mixed with other gases.[1]

Excepting oxygen and silicon, combined hydrogen is the most widely diffused element in nature; it forms 11 per cent. of the weight of water and enters into the composition of all vegetables and animals, many minerals and industrial products, petroleum, etc. Almost 1 per cent. of the weight of the subaqueous globe consists of hydrogen.

PHYSICAL PROPERTIES. Pure hydrogen is a colourless and odourless gas; it is not respirable when pure, but is harmless when mixed with air.

Its density, compared with air, is 0·06947 (Rayleigh, 1893), and it is thus 14·43 times lighter, and can be poured from one vessel to another. Small balloons of collodion or soap-bubbles filled with hydrogen rise rapidly in the air. Its density is normal even at a white heat, so that it does not undergo dissociation, as is the case with chlorine, iodine, etc. After allowing for all corrections, a litre of hydrogen weighs 0·09009 grm. at normal temperature and pressure (Rayleigh, 1895).

Hydrogen has a greater specific heat (3·410) and is a better conductor of heat than any other gas (about seven times as good as air). It is also a good conductor of electricity, as can be shown by the following experiment:

A platinum wire is stretched inside a glass tube, a current of air being then passed through the tube, and an electric current simultaneously passed through the wire from four Bunsen cells. The wire glows, because the air surrounding it is a poor conductor of electricity. The electric current is now stopped and hydrogen passed through the tube for some minutes to drive out all the air, in order to avoid all danger of explosion. If the current is again passed through the platinum wire the latter does not glow, because the hydrogen which now surrounds it is a good conductor of electricity.

The spectrum of hydrogen gas consists of four luminous lines, of which the two most characteristic are red and greenish blue.

This gas is the most readily diffusible known, because it is the lightest; it diffuses through substances which are only slightly porous, such as rubber, and at high temperatures even through quartz vessels. It is absorbed in large quantities by porous bodies—and condensed in the pores—in increasing amount as the temperature is lowered and the pressure raised, so-called solid solutions being formed (see Part III: Alloys).

It is very slightly soluble in water (1·93 vols. in 100 vols. of water); 100 vols. of alcohol dissolve 7 vols. of hydrogen, while 100 vols. of petroleum dissolve 65 vols.

The occlusion or absorption of hydrogen by heated metals is especially

---

[1] The gas of the intestines of the ox consists partly of hydrogen, and contains also about 70 per cent. of methane; these gases are formed by the decomposition of cellulose rendered partly soluble by certain enzymes secreted by the special micro-organisms of the intestine (*see* Vol. II., "Organic Chemistry"). During the respiration of seeds and moulds hydrogen is also formed. The hydrogen of the air (up to 20 c.c. per 100 litres) is derived partly from the action of ultra-violet rays on sea-water and on the aqueous vapour of clouds ($2H_2O = H_2O_2 + H_2$).

great in the case of platinum, nickel, and cobalt (at 400°). Palladium, according to Graham, absorbs 376 vols. at the ordinary temperature and almost double that amount at about 100°. On using palladium as the cathode in electrolysis this metal absorbs 935 vols. (cathodic, active, or metallic hydrogen). Two-thirds of this hydrogen is found to be combined, forming palladium hydride [Troost and Hautefeuille (1875) and Krakau], and the other third is dissolved in the hydride forming an alloy or solid solution in the proportions represented by Pd_3H_2 (Mond, Ramsay, and Shields, 1901). A colloidal solution of palladium absorbs 420 vols. of hydrogen, which it renders active; Paul (1910) based a method for the determination of hydrogen on this fact.

Hydrogen in the liquid state was first obtained in large quantity by Dewar in London in 1898 at a pressure of 180 atmospheres in the apparatus shown in Fig. 38 (Cailletet and Pictet claim to have liquefied it in 1877, but the characters attributed to it by them were incorrect):

The hydrogen, obtained from a cylinder, *A*, at a pressure of 180 atmospheres, is cooled in the first spiral tube, *B*, with solid carbon dioxide; in the second spiral, *C*, it is then cooled with liquid air to about — 190°, and, finally, in the third spiral, *D*, by making use of the great refrigeration produced by the rapid expansion of the same hydrogen, compressed to 180 atmospheres, when the valve, *F*, is opened, the temperature is lowered to — 232°, and a jet of liquid hydrogen issues from the aperture, *E*.

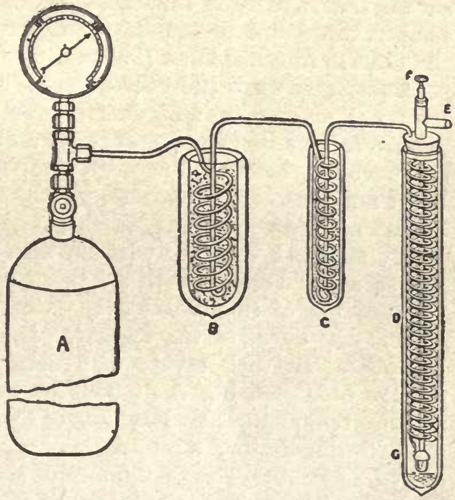


FIG. 38.

Liquid hydrogen is limpid, colourless, and highly refractive and dispersive. It shows no absorption spectrum. It boils at — 252·6° at the ordinary pressure (that is, at 20·4° on the absolute scale). At this temperature all known gases and liquids become solid except helium, which does not liquefy even at — 260°.

The density or specific gravity of liquid hydrogen is 0·070, and it is the lightest liquid known, being fourteen times lighter than water.

When the pressure above liquid hydrogen is rapidly reduced, the temperature is lowered to — 258·9°, and the hydrogen solidifies. The lowest temperature obtained by evaporating solid hydrogen was — 260° (that is, 13° absolute) and the specific gravity of solid hydrogen is 0·0763 (Dewar, 1904).

CHEMICAL PROPERTIES. Free hydrogen combines directly with fluorine even at — 23,° whilst with chlorine it unites only under the action of light or heat; with bromine both light and heat are required, whilst with iodine it combines very slowly under the influence of light and heat, but if condensed in spongy platinum it combines immediately, acting like nascent hydrogen. The affinity of hydrogen for the other elements diminishes with increasing atomic weight of the latter; for example, it unites with oxygen with explosion, with sulphur the reaction is incomplete and occurs in presence of pumice stone, with tellurium cathodic hydrogen is required (electrolytically nascent), etc.

Two grams of hydrogen, combining with 16 grms. of oxygen to form liquid water, develop 68,400 cals. (286 Kj.). The flame of hydrogen burning in pure oxygen reaches a temperature of over 2800° (that of carbon monoxide in oxygen gives 2600° and of acetylene in oxygen 3000°).

Hydrogen is a combustible gas, but does not support combustion. Thus, it burns well in air with a colourless flame, but a burning substance immersed in it ceases to burn. Under certain circumstances it does, however, support combustion, *e. g.*, it maintains the combustion of a chlorine flame. It is not poisonous when respired in large amount, but, as was shown by Fontana in 1780, it causes asphyxiation.

On introducing a small hydrogen flame into glass tubes of different lengths and widths very varying notes are produced, forming the so-called *chemical harmonica ;* this is due to numerous small explosions which succeed one another regularly and rapidly in the tubes through the combination of the hydrogen with the oxygen of the air.

Hydrogen is an energetic reducing agent, because it replaces or eliminates the oxygen of many compounds in the form of water. Thus, for example, on passing hydrogen over red-hot copper oxide, pure copper and water are formed : $CuO + H_2 = Cu + H_2O$.

By the term *reduction* is ordinarily understood the elimination of oxygen from a compound, with or without substitution by hydrogen. Ipatiev (1909) has shown that hydrogen separates metals from solutions of their salts at high temperatures and pressures, for example, it separates metallic copper from the acetate in solution at 120° and 600 atmospheres pressure.

Enormous quantities of nascent hydrogen, produced by the action of hydrochloric acid on zinc dust or iron turnings, are used in the manufacture of various organic compounds, *e. g.*, aniline, phenylenediamine, naphthylamine, etc., from the corresponding nitro-compounds (*see* Vol. II., "Organic Chemistry"). Large amounts of hydrogen are now also used for the conversion of fish oils into consistent fats.

By mixing 2 vols. of hydrogen with 1 vol. of oxygen one obtains *detonating gas*, so called because with a lighted substance it gives a powerful explosion. The product of this reaction is water vapour which condenses very rapidly, so that the effect of the explosion is to some extent weakened. On mixing 10 vols. of air with 4 vols. of hydrogen the right proportions for detonating gas are obtained, but even with 10 vols. of air and 3 vols. of hydrogen the mixture still explodes. Mixtures of hydrogen and oxygen are explosive within the following limits : a minimum of 8 per cent. and a maximum of 64 per cent. of hydrogen; below the minimum or above the maximum the mixture does not explode. The temperature of ignition of detonating gas is about 700°.

Hydrogen produced by the fermentation and putrefaction of organic substances is chemically very active, as also is that produced in the nascent state from sodium amalgam or that occluded in palladium; this hydrogen is not in the molecular, but probably in the atomic state. In this condition it is an energetic reducing agent, and when hydrogen is greatly compressed it is also much more active and reduces even mercuric chloride : $HgCl_2 + H_2 + 100$ atmos. pressure $= Hg + 2HCl$. This phenomenon is quite common, as has been shown by Ipatiev (*vide supra*).

Of interest is the formation of metallic hydrides, some of which are of industrial importance, *e. g.*, in the manufacture of hydrogen. The following are well known : K_2H, KH, NaH, CaH_2, SrH_2, BaH_2, MgH_2, Cu_2H_2, P_2H_2, and PdH. A. Stock (1912) prepared boron hydrides, analogous to the hydrocarbons : B_2H_6, B_4H_{10}, B_6H_{12}, and $B_{10}H_{14}$, and zirconium hydride, ZrH_4, analogous in composition to methane, has also been obtained.

INDUSTRIAL USES OF HYDROGEN. This gas is valuable on account of the high temperature produced when it is burnt in the presence of oxygen (up to 2800°), and is made use of in the oxy-hydrogen blowpipe (*see* Oxygen) for the fusion and welding of platinum, iron, lead, copper, etc. Hydrogen and oxygen obtained from two cylinders of the strongly compressed gases are brought together in a single tube and when ignited form the oxy-hydrogen flame.

The *oxy-hydrogen flame* has an oxidising action if oxygen is present in excess and a reducing action when an excess of hydrogen is present (5 vols. hydrogen and 1 vol. oxygen); it is neutral if exactly 1 vol. of oxygen is present to each 2 vols. of hydrogen. Ordinarily, for welding metals, a flame is used containing 3 to 4 vols. of hydrogen to 1 vol. of oxygen, and for welding lead (for example, in lead chambers for the manufacture of sulphuric acid) the hydrogen flame is fed with air. For some years the oxy-hydrogen flame has been advantageously replaced by the oxy-acetylene flame (*see* Oxygen); with equal volumes of acetylene and oxygen, temperatures of 3500° may be obtained.

Hydrogen is used in steel-works for the autogenous welding of iron to iron and for homogeneously filling up, with a perfect joint, the blow-holes which are often found in molten steel castings. The welding is much more perfect than that obtained with the electric arc, which is also rather inconvenient because its intense light is very trying to the sight of the workmen, and produces bad headaches.

In making boilers and tanks the superposed iron plates were formerly riveted and then caulked; recently autogenous welding has been applied, with great economy of time and money, and more especially for vessels which have not to support high gaseous or liquid pressures.

Hydrogen and also water gas (*see below*) are used for heating the baking and annealing kilns for ceramic materials.

Many chemical operations can be carried out by means of the oxy-hydrogen flame instead of the electric furnace; for instance, the conversion of barium carbonate into barium oxide appears to be moderately well effected.

In glass-works the heating of furnaces and crucibles is greatly accelerated by the oxy-hydrogen flame.

Limelight is produced by impinging an oxy-hydrogen flame on to a block of quicklime. In this way a very vivid light is obtained, which is often used for lighthouses and for projection lanterns in place of the electric arc. The Döbereiner lamp is of historical interest only, and consisted of a bottle in which hydrogen was evolved and then passed over platinum sponge, causing this to glow and thus igniting the gas.

During the last few years hydrogen has acquired new and great importance in aeronautics (now that the problem of dirigibles has been definitely and successfully solved) for filling balloons, because, compared with coal-gas, hydrogen is much lighter, and when compressed in steel bottles to 200 or even 300 atmospheres pressure, it occupies little space and is convenient for transport; also it can be prepared on the spot, as will be shown below. The ascensional force of hydrogen is given theoretically by the difference in weight between a cubic metre of air and a cubic metre of hydrogen (1·293—0·090 kilo), and is thus 1·203 kilos, but allowance must be made for the lesser weight of the air at high altitudes (at the Margherita Observatory, on Monte Rosa, the altitude is 4559 metres and the atmospheric pressure about 440 mm.) and for the greater weight of hydrogen as prepared, in the wet state (about 0·120 grm. per cubic metre). In practice one kilo is taken as the raising capacity of one cubic metre of hydrogen, and it is then easy to calculate the volume required to raise a given weight (balloon, car, crew, etc.). When coal-gas (1 c.m. = about 0·5 kilo) is used, the theoretical ascensional power is only 700 grams per cubic metre. For aeronautics it is important that the arsenic hydride present as an impurity should be eliminated, as in some cases it may produce poisoning of the crew, followed by death (at Chalais, on April 3, 1900, two people were killed and three others seriously poisoned); for this reason it should be stipulated that the sulphuric acid used for producing the hydrogen contain not more than 10 centigrams of arsenic and 1 gram of antimony per litre.[1]

Hydrogen is used indirectly for illumination, with the Auer mantle, and as a motive force, being an important component of water-gas (together with CO_2 and CO) and of lighting gas.

Much hydraulic power which is still lost in waterfalls, especially at night, could be profitably employed for the electrolytic decomposition of water; the two separate gases, collected in gasometers, could be kept till the daytime, and then used as a source of heat and thus also of mechanical power.

Oxy-hydrogen gas is perhaps destined to replace coal in great part for many industrial purposes, as coal-gas is inferior as a source of heat and in some cases is 20 per cent. dearer.

In 1905 the engineer Sanne proposed the use of compressed and heated hydrogen for gas motors, its force of expansion being greater than that of other gases under the same conditions. This he deduced from the fact that Boyle's law and the efficiency of Carnot's cycle, in the case of compressed and heated gases, are not equal for all gases, and that the specific constants of the individual gases, deduced from the thermodynamic equations connecting the specific heats at constant pressure and constant volume, indicate the thermodynamic value of the hydrogen to be greater than that of all other gases.

Electrolytic hydrogen is placed on the market in steel cylinders of 35 litres capacity (or more) at 200 atmospheres pressure. Also for the railroad transport of hydrogen in large quantities, especially for military purposes, suitable wagons holding 40 cylinders each have been constructed. Owing to repeated explosions in various countries, the pressure used has been lowered from 200 to 150 and now to 130 atmospheres. Steel cylinders 2 metres long and holding 40–46 litres weigh about 75 kilos and, at a pressure of 150 atmospheres, contain 6–7 cu. metres of hydrogen.[2] Compressed hydrogen is sold at about 10*d.* per cu. metre, measured at the ordinary pressure. Some of the large German electrolytic soda-works sold hydrogen (before the war), compressed at 150 atmospheres, for about 1½*d.* per cu. metre. Further, the hydrogen made from water-gas by the Frank-Caro-Linde process (*see* later) now costs about 1½*d.* per cu. metre and contains only 0·5 per cent. of CO. The electrolytic process is practicable when the hydrogen is a by-product and the greater expenses are borne by the chlorine, oxygen, and caustic soda.

In Italy 42,000 cu. metres of compressed hydrogen were produced in 1905, more than

---

[1] In the filling of dirigibles account must be taken of loss and escape of the gas, these being reckoned at about 2–4 per cent. when the vessels are at rest, although they may reach or exceed 25 per cent. when the dirigibles are in use and may have to fly very high to escape clouds; weather conditions also influence the losses.

The gas in the envelope gradually changes in composition, and hence in ascensional power, owing to part of the gas either issuing from valves under the influence of the sun's rays or diffusing spontaneously through the fabric and to a corresponding, though lesser, entry of air. A commercial pure hydrogen containing 98·5 per cent. H, 1·23 per cent. N and 0·27 per cent. O, had the sp. gr. 0·087 and the ascensional power 1181 grams per cu. metre. When it was used to fill a vessel 6500 cu. metres in capacity (length 80 metres and maximum diameter 14 metres) it showed, after 8 days and 4 journeys with exposure to the sun, the composition (ignoring the diminution in volume): 94·9 per cent. H, 4·4 per cent. N, and 0·7 per cent. O. After a fresh quantity of 1100 cu. metres of hydrogen had been added 7 voyages were made during a period of 12 days, the composition of the gas being then: 93·7 per cent. H, 5·33 per cent. N, and 0·97 per cent. O. To restore the original lifting power, 1150 cu. metres of hydrogen would then be necessary.

In the gas contained in these vessels strata of slightly varying composition form, owing principally to the diffusion phenomena at the periphery.

[2] In Germany the regulations for the transport of compressed and liquefied gases are as follows: for nitrous oxide, the volume of the steel cylinder should be 1·34 litres per kilo of gas; for liquid ammonia, 1·86 litres per kilo; for liquid chlorine or nitrogen tetroxide, 0·8 litre per kilo; for sulphur dioxide or phosgene, 0·8 litre per kilo; for methyl ether, 1·65 litres per kilo; for methyl- or ethyl-amine, 1·7 litres per kilo; for methyl or ethyl chloride, 1·25 litres per kilo; for liquid ethane, 3·3 litres per kilo, and for any other liquefied gas, 3·5 litres per kilo. The maximum pressure allowable at 15° is 20 atmos. for gaseous carbon dioxide; 15 atmos. for acetylene absorbed by porous materials impregnated with acetone; 2 atmos. for liquefied acetylene; 10 atmos. for slightly compressed, and 125 atmos. for highly compressed oil gas; 200 atmos. for oxygen, hydrogen, illuminating gas, nitrogen, or air.

43,000 cu. metres in 1907, and only 38,000 cu. metres, of the value of £1720, in 1908; the diminution in consumption is due to the replacement of the oxy-hydrogen blowpipe by oxy-acetylene for welding. In 1910 the German electrolysis works (caustic soda and potash) produced 10 million cu. metres of hydrogen, and in 1913 were granted a permit for railway transport of the gas by means of wagons carrying 32 large iron cylinders holding 2000 cu. metres of compressed gas. The Elektron works at Griesheim and Bitterfeld, which use 15,000 h.p., produce 7 million cu. metres of hydrogen per annum, *i. e.*, 20,000 cu. metres per day, the gas being distributed by means of a network of tubes 4500 metres in length.

PREPARATION IN THE LABORATORY. In the sixteenth century Paracelsus already knew that some metals, in contact with certain dilute acids, developed an inflammable gas (*inflammable air*). In 1766 Cavendish succeeded in distinguishing and separating hydrogen from other inflammable gases, and in 1781, together with Watt, showed that the sole product of the combustion of hydrogen is water.

In 1781 and 1783 Lavoisier prepared hydrogen by decomposing water with red-hot iron, by which means he was able to confirm fully the chemical composition of water, both from the synthesis of Cavendish and from his own analysis.

Hydrogen is commonly obtained in the laboratory by the action of dilute hydrochloric or sulphuric acid (one part of concentrated hydrochloric acid and two of water, or one of sulphuric acid and four of water) on small pieces of zinc (or iron):

$$Zn + H_2SO_4 = H_2 + ZnSO_4; \quad 2HCl + Zn = ZnCl_2 + H_2.$$

For this operation a Kipp generator, as illustrated in Fig. 39, is usually employed; the two lower glass bulbs, *b* and *d*, are in one piece and in communication; the upper bulb, *c*, which terminates below in a long glass tube, communicates directly with the lowest bulb, closing hermetically on to the neck, *c*. Into the middle bulb, *b*, granulated zinc (obtained by pouring molten zinc into water) is introduced through the aperture, *e*, and the dilute acid is poured into the upper bulb so that it also fills the lowest bulb and is driven into the central one, where, in contact with the zinc, it produces hydrogen. The gas escapes from the aperture, *e*, provided with a cock, is washed by bubbling through a solution of caustic soda in the bottle, *S*, and is collected over water in the cylinder, *C*. When the evolution of gas is to be stopped the cock, *e*, is closed, and the gas which continues to be developed in *b* exerts pressure on the acid and drives it into the lowest bulb, *d*, and partly into the uppermost bulb. When there is no more acid in the middle bulb evolution of gas ceases, and when gas is again required the cock is opened and the acid once more comes into contact with the zinc. By using this ingenious apparatus any quantity of gas (*e. g.*, hydrogen sulphide, carbon dioxide, acetylene, etc.) can be produced at any time by a reaction between a liquid and a solid substance without any loss of time or waste of reagents. In order to avoid the formation of explosive mixtures in the apparatus, the hydrogen must be allowed to escape until all the air has been expelled; the gas collected in a small test-tube should not explode when lighted.

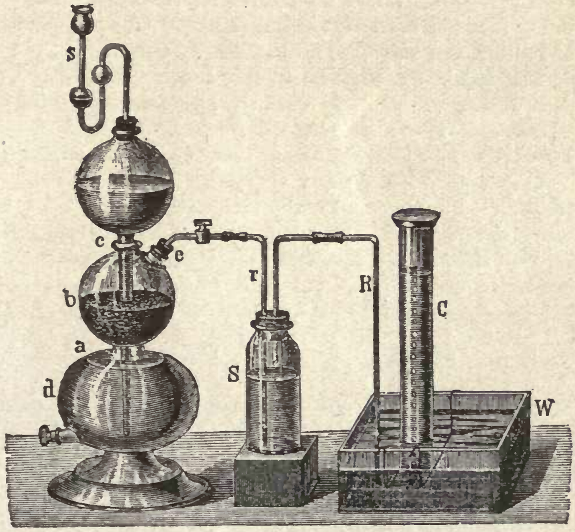


FIG. 39.

Another apparatus, more simple and equally convenient and in general use, is shown in Fig. 40, and consists merely of two tubulated bottles, *S* and *Z*, communicating below by a long rubber tube, *r*. One of these contains the zinc and the other the acid; when the latter bottle is raised, acid passes into the former and the gas is developed; when it is lowered, the acid runs back and the evolution of gas ceases.

During the electrolytic decomposition of water (acidified with sulphuric acid, 1 : 10) the hydrogen collects at the negative pole, and the oxygen at the positive pole. Bunsen proposed an apparatus for collecting the purest electrolytic hydrogen (Fig. 41) from acidified water by separating the oxygen at the positive pole with a plate of amalgamated zinc and collecting the hydrogen from the negative pole and leading it through a tube which is fitted in the top of the apparatus and surrounded by water or mercury to prevent escape of the gas.

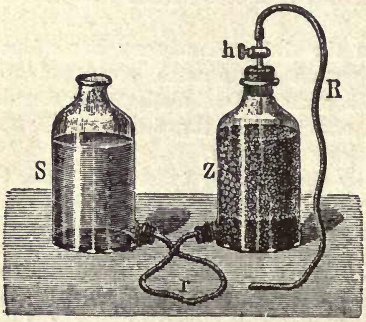


FIG. 40.

Hydrogen is purified by washing with a solution of potassium permanganate, and dried either with fused potassium hydroxide or by being bubbled through concentrated sulphuric acid.

Hydrogen is also obtained by the electrolysis of a dilute aqueous solution of sodium hydroxide, but in this case it is always contaminated with small traces of acetylene derived from the small quantities of carbides contained in the caustic soda; this applies in a still greater degree to potassium hydroxide. Hydrogen so obtained contains only 0·001 to 0·005 per cent. of nitrogen.

Hydrogen is formed by the action of various metals on water; potassium acts even in the cold and takes fire; sodium acts less violently, and in the form of amalgam (an alloy of sodium and mercury) gives a steady current of gas: $H_2O + Na = NaOH + H$.

The alkaline earth metals also develop hydrogen with water. In all these cases the hydroxides of the metals and free hydrogen are formed. Magnesium powder commences to react with water, evolving hydrogen at 70°, the action being intensified in presence of a little magnesium chloride, which dissolves the magnesium oxide formed at the same time.

Iron decomposes steam at high temperatures with formation of hydrogen, this reaction commencing at 300°, and attaining a maximum at 800°:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

This method was formerly used on an industrial scale, but was afterwards abandoned; it has recently come into use again for the manufacture of large amounts of hydrogen, the iron being regenerated by treatment with carbon. Hydrogen thus obtained costs about 1½*d.* per cu. metre. If the reaction is carried out under a pressure of 300 atmospheres and in presence of ferrous chloride (catalyst), hydrogen of 99·95 per cent. purity is obtained at a cost of about 1·2*d.* per cu. metre (Bergius, 1913).

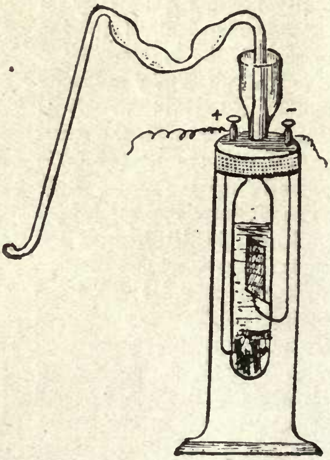


FIG. 41.

The hydrogen formed is collected by displacement of water in glass cylinders inverted over a vessel of water. It is recognised by burning with a pale flame, forming water, when lighted.

Hydrogen is obtained fairly pure and in abundance by the action of powdered aluminium on boiling water, with the help of the catalytic action of a little dilute potassium permanganate solution. After the action has been started it continues without further heating. Permanganate in excess is harmful and cannot be replaced by other oxidising substances such as chlorates, perchlorates, or potassium nitrate.

Pure hydrogen is also obtained by heating potassium formate with potassium hydroxide:

$$\underset{\text{Potassium formate.}}{CO_2KH} + KOH = \underset{\text{Potassium carbonate.}}{CO_3K_2} + H_2.$$

This hydrogen is dry and very active, and is able to transform various metals into their hydrides. Also zinc and magnesium evolve hydrogen from ammonium salts, excepting the nitrate.

Hydrogen may be obtained by the action of zinc on strong alkali solutions (best in presence of iron): $Zn + 2KOH = Zn(OK)_2 + H_2$, or by heating finely divided zinc or iron to redness with a mixture of quicklime and slaked lime: $Fe + Ca(OH)_2 = FeO + CaO + H_2$.

Very pure hydrogen can be obtained from pure zinc and pure sulphuric acid, but as chemically pure zinc alone does not react with the pure acid a small trace of platinum chloride must be added; this produces a minute deposit of platinum on the zinc, forming a voltaic couple, which causes the gradual solution of the zinc and regular evolution of pure hydrogen (which can only contain the traces of other gases occluded in the zinc).

PURIFICATION OF HYDROGEN. Hydrogen prepared from ordinary reagents always contains impurities, such as the nitrogen oxides, N_2O and NO (produced from the nitrous products contained in the sulphuric acid), hydrogen sulphide (H_2S), sulphurous acid (SO_2), hydrogen phosphide (PH_3), arsenic hydride (AsH_3), and carbon monoxide (CO) and dioxide (CO_2). It is purified by washing with a 5 per cent. solution of silver nitrate, and then by sodium hydroxide solution, and is finally dried by passing over phosphoric anhydride. If copper sulphate is added to the zinc, H_2S does not occur as an impurity. CO_2, H_2S, and SO_2 may also be absorbed by ammonia; AsH_3 and PH_3 are removed by fuming nitric acid or by bromine, and the nitrogen oxides by ferrous sulphate.

A satisfactorily complete purification for industrial purposes is obtained with an alkaline solution of potassium permanganate (5 grams of permanganate in 100 grams of 10 per cent. potassium hydroxide solution). Hydrogen is sometimes purified by passing it through vessels containing quicklime, iron oxide, and sawdust (Laming's material, as used for purifying coal-gas). In a prize competition at Frankfort in 1906 the method of Wentzki was recognised as the most reliable for eliminating arsenic hydride; in this method the gas is passed into a cylinder of one-half of the volume of the generator, containing a mixture of two parts of dry calcium hypochlorite with one part of moist sand or other finely divided material.

Hydrogen may be considered to be well purified when it gives no precipitate or coloration on passing through a solution of silver nitrate. When dry hydrogen is required it must be finally passed through quicklime, concentrated sulphuric acid, or granulated fused calcium chloride.

INDUSTRIAL PREPARATION OF HYDROGEN. Of the many various processes which have been proposed for the preparation of hydrogen on the large scale, we shall record only those which have been successfully applied.[1]

---

[1] The preparation of hydrogen on a large scale was already tried without success by Fontana in 1782, by the action of steam on red-hot iron: $3 Fe + 4H_2O = Fe_3O_4 + 4H_2$. This process was taken up again by Giffard in 1788, but was very soon abandoned. Oettel, according to his Eng. Pat. 16,759 of 1885, prepared hydrogen by passing steam over iron scrap and filings enclosed in strongly heated iron tubes which had been evacuated. In 1887 Belou (Ger. Pat. 43,989), in Paris, prepared pure hydrogen by passing steam over red-hot iron tubes or bars enclosed in a retort. The oxide of iron which was formed was afterwards reduced to metallic iron by sprinkling it with powdered coal and re-heating. A mixture of CO and CO_2 was thus formed which was used for heating the retorts.

Howard-Lane, and also Elworthy and H. Williamson (1902), attempted to make this process industrial by patenting a special form of furnace in which the iron was disposed in thin layers in channels of refractory material, so that the surface of the iron was traversed by the steam (Ger. Pat. 164,721). In a French patent of 1909 (No. 405,200) the use of iron obtained by the reduction of the oxide (burnt pyrites) is proposed; this material, being finely divided, gives a better yield. The resulting iron oxide is reduced each time to metallic iron by means of water-gas (H and CO) of which the carbon monoxide is absorbed at 180° by a mixture of lime and potassium hydroxide ($KOH + CO = HCO_2K$); the resulting potassium formate yields hydrogen on heating to 300° ($HCO_2K + KOH = K_2CO_3 + H_2$). This process is used for military balloons at Berlin, and the working costs are less than 1·8*d.* per cu. metre of hydrogen; the cost of prime materials does not raise the total cost much.

W. Majert and G. Richter, in 1888, prepared hydrogen by a process based on the principle of

In 1904 Moissan and Siemens found that, when silicon is heated with aqueous caustic soda solution, hydrogen is evolved in amount more than corresponding with the equation: $2NaOH + H_2O + Si = SiO_3 Na_2 + 2H_2$. On an industrial scale, however, the reaction slackens after a short time, and only 80 per cent. of the available hydrogen is obtained. According to the German patent No. 216,768 of 1908 and the French patent No. 406,930 of 1909, however, an almost theoretical yield is obtainable if a dilute (8 per cent.) caustic soda solution is heated with 14 per cent. of calcium hydroxide and 7 per cent. of silicon; the sodium silicate (Na_2SiO_3) remaining in solution is also of value. A special apparatus was constructed by F. Jaubert for this process (German patent No. 262,635 of 1910); the production of 100 cu. metres of hydrogen requires 63 kilos of silicon and 180 kilos of caustic soda. Owing to the price of the silicon, the hydrogen costs four to five times as much as that from water-gas.

The German Zeppelins are also charged with hydrogen prepared by decomposing compressed acetylene by means of the electric spark, carbon (smoke black) being deposited and hydrogen liberated.

The same reaction, $C_2H_2 = C_2 + H_2$, used in 1881 by Berthelot and Vieille for the explosion of mixtures containing acetylene, was put on an industrial basis by F. Morani (German patent No. 141,884 of 1901) by means of an apparatus in which a mixture of 4 vols. of acetylene and 1 vol. of air at a pressure of 6–8 atmos. was exploded by an electric spark, the pressure then increasing to 15–50 atmos. For each kilo of smoke black, 1 cu. metre of hydrogen, costing about 2*d.*, is obtained. The process was improved by Machtole (German patents No. 194,939 of 1905 and No. 212,345 of 1908), who provided the Zeppelin Company with 200,000 cu. metres of hydrogen of 98 per cent. purity per annum—for filling Zeppelins, each holding 20,000 cu. metres; in July 1910 there was a serious explosion, but the plant was renewed with a capacity of 2000 cu. metres per day.

For filling small balloons use is made of calcium hydride—proposed by Moissan in 1908—which, in contact with water, gives a very vigorous evolution of hydrogen: $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$; the calcium hydride is stored under petroleum. To obtain 100 cu. metres of hydrogen, 95 kilos of 100 per cent. hydride or 113 kilos of 84 per cent. hydride are required.

During the grand manœuvres in France in 1911, a balloon holding 2400 cu. metres was filled in two hours by means of 2500 kilos of calcium hydride (at 4*s.* per kilo); the latter occupied a space of about 1·5 cu. metres, while 10–12 cu. metres of water are required per 1000 cu. metres of gas.

In some chemical industries, and for filling balloons in stationary military camps, hydrogen was prepared some years ago by the action of dilute sulphuric acid on iron turnings. For this purpose strongly bound and perfectly gas-tight vats are used: $Fe + H_2SO_4 = FeSO_4 + H_2$.

The inconvenience of this process arises from the fact that the iron finally becomes covered with ferrous sulphate which protects it from the further action of the acid. Among the many ingenious mechanical devices for eliminating this difficulty the column devised by Renard has met with success. This removes the ferrous sulphate gradually as it is

---

that of Tissié du Motay and Maréchal from lime and coal: $C + 2Ca(OH)_2 = 2CaO + CO_2 + 2H_2$; in order to accelerate the reaction they improved it by employing a mixture of zinc dust with calcium or magnesium hydroxide or similar substances: $Zn + Ca(OH)_2 = ZnO + CaO + H_2$. In this way no carbon dioxide was formed but only hydrogen. The lime and zinc were enclosed in small boxes which on heating quickly evolved hydrogen; these were used for military purposes and for rapidly filling balloons in time of war. This process, which attracted much interest, cannot be thought of in practice owing to its enormous cost; 1 cu. metre of hydrogen introduced into the balloon costs 4*s.* In 1888 Jacoby proposed the replacement of the zinc by iron, by which means one-third more hydrogen is obtained of purer quality, and free from arsenic, at less cost.

formed by means of a continuous circulation; sulphuric acid of 12 — 16° Bé. enters at the base of a lead cylinder containing iron turnings, and the ferrous sulphate solution, which no longer contains sulphuric acid, is continuously discharged at the top; the gas is washed with water, then passes over Laming's mixture (*see* Coal-gas, Vol. II., "Organic Chemistry") to remove sulphur compounds, and is freed from other acids by passing over granulated sodium hydroxide. For the preparation of 600 cu. metres of hydrogen, 1800 kilos of iron, 3000 kilos of sulphuric acid of 66° Bé., and 100 cu. metres of water are required. If zinc is used instead of iron 2100 kilos of this will be required, with 3600 kilos of sulphuric acid. The sulphuric acid should not contain more than 10 centigrams of arsenic and 1 gram of antimony per litre, and to avoid arsenic in the metal steel turnings are used.

In the Russo-Japanese War (1904–1905) the Russians found it convenient, in order to avoid the transport to and fro of heavy steel cylinders of compressed hydrogen for their balloons on the field of battle, to produce hydrogen as required on the spot (in Manchuria) by the action of 30 per cent. caustic soda solution on aluminium scrap. The former was contained in cylinders of sheet iron 2 metres long and 0·5 metre wide, in which a metallic box containing the aluminium, in the form of sheets of 1·5 to 2 mm. thickness, was immersed: $Al + 3NaOH = Al(ONa)_3 \times 3H$. For 100 cu. metres of hydrogen 81 kilos of aluminium and 310 kilos of caustic soda are required. As the gas so obtained was very warm it was cooled and washed by passing through cylinders of water. The process is, therefore, only of service where there is an abundant supply of water. With twenty-four generators and six coolers a balloon of 400 cu. metres capacity can be filled in half an hour. The generators and washers can be carried on the backs of fifteen horses, and a further thirty to fifty horses are required to transport the balloon and accessories, including the chemicals (KOH and Al). In the Boer War the British employed hydrogen compressed to 200 atmospheres in steel cylinders, fifty horses being required for the transport of all materials for a balloon of 400 cu. metres, apart from the transport of the cylinders to and from England.

A. Frank and N. Caro (German patents Nos. 112,416, 132,836, 174,324, 174,846 of 1904–1906) obtain moderately pure hydrogen by passing dry water-gas, containing up to 50 per cent. of hydrogen and 40 per cent. of carbon monoxide (*q. v.*), over calcium carbide at above 250°: $2 CaC_2 + 2CO = 2CaO + 6C$ (graphite). In order to save carbon, the water-gas is first passed over calcium hydroxide to fix the carbon dioxide and over cuprous chloride to fix carbon monoxide; the remaining gas, containing 90 per cent. of hydrogen, is passed over the carbide heated to 800–900°, hydrogen of 99–99·6 per cent. purity being obtained. Since the revivification of the cuprous chloride is not easy, Frank obtains 96 per cent. hydrogen by passing water-gas directly into a Linde liquid air machine, where the CO_2, CO, and N are liquefied and separated (90 per cent. CO is obtained and is utilised by combustion in a gas engine).

G. Claude liquefies illuminating gas (which contains up to 50 per cent. of hydrogen) by means of a liquid air machine, the hydrogen alone remaining gaseous at —193°. Others prefer to pass illuminating gas or oil gas into a cylinder containing incandescent coke at 1200°, thus decomposing the hydrocarbons; this yields hydrogen containing a little carbon monoxide,[1] and the lifting power is increased from 0·76 to 0·95 kilo per cu. metre of gas which costs about 1·5*d.* and contains 80·7 per cent. H, 6·9 per cent. CH_4, 7·3 per cent. CO and 5·1 per cent. N (process of Oechelhäuser, Dessau).

---

[1] According to a German patent of 1913, carbon monoxide may be separated from hydrogen by heating the mixture at 150–225° in presence of caustic soda under a pressure of 50 atmos. Another patent (Siemens and Halske, 1908) specifies the treatment of hot calcium carbide with steam: $CaC_2 + 5H_2O = CaO + 2CO_2 + 10H$. The Griesheim factory has obtained hydrogen from moist water-gas by heating it at 400–500° with calcium hydroxide which, as Merz and Weith showed in 1880, fixes carbon monoxide: $CO + Ca(OH)_2 = CaCO_3 + H_2$. This process is well fitted for use at stations which supply hydrogen for dirigibles. A slight excess of steam is required and the temperature must not rise above 500° (the reaction is exothermic), since, if much calcium oxide is formed, carbon separates without formation of hydrogen: $CaO + 2CO = CaCO_3 + C$. The Griesheim Elektron Co. supplied to the German military service 70,000 cu. metres of hydrogen in 1901, more than 185,000 in 1905, and 610,000 in 1909.

For filling Zeppelins in Germany steam is also decomposed directly by means of wood charcoal impregnated with sodium silicate and potassium carbonate, this being dried, mixed with lime, and heated at 450° in vertical retorts, into which is passed steam superheated to 400°.

In 1910 Ostromislenski and Burschanadze prepared a new light gaseous mixture for balloons by heating mazut (petroleum residues) vapour at 700° in presence of catalytic nickel; the resulting gas contains 75 per cent. of H, 28 per cent. of gaseous hydrocarbons, and 1·7 per cent. of CO, 40 per cent. of coke remaining.

INDUSTRIAL ELECTROLYTIC METHODS. For the production of large quantities of hydrogen electrolytic methods are commonly used to-day, as they give a comparatively cheap product. The Englishmen, Carlisle and Nicholson, in 1800, were the first to decompose water electrolytically, using a Volta pile. The method has acquired practical importance only during the last few years.

In electrolysis the two gases are collected separately: oxygen at the positive, and hydrogen at the negative pole; if, however, the electrodes are in close proximity the gases are able to mix to some extent, so that it is necessary to separate the electrodes by means of a diaphragm. The latter, however, causes various difficulties (such as high resistance, short life, liability to obstruction, etc.) unless suitable material is chosen. Porous porcelain, asbestos fabrics, parchment paper, glass, rubber, etc., have all been tried, and after many attempts the practical solution was found by the brothers Garuti, who employed metallic diaphragms. The objection was at first raised that if the metallic diaphragm became polarised and took part in the electrolysis, the face opposite the anode (which develops oxygen) would evolve hydrogen, and the other face oxygen, and the explosive mixtures thus formed would constitute a serious danger. This difficulty is avoided in practice in the following manner: the electromotive force (E.M.F.) necessary to decompose water is about 1·5 volt, and when the diaphragm is polarised the whole system represents two cells in series; therefore, if the diaphragm is to play any part in the electrolysis, double the electromotive force, *i. e.*, 3 volts, is required ($1\frac{1}{2}$ volt for each side) If the terminals of the cell are maintained at an E.M.F. of less than 3 volts electrolysis can only take place at the electrodes and the diaphragm remains neutral.

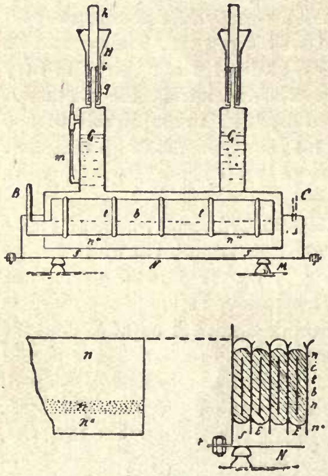


FIG. 42.

These difficulties having been quite overcome by the Garuti system, it was tried for the first time in 1890 in the Brera Palace, in Milan, and was then at once applied on a vast scale in the gun factory at Terni, in the Milan steel foundry, in the military aeronautical camp at Rome, and later in other Italian and foreign establishments (especially by Garuti and Pompili at Tivoli). Great care is always necessary that no mixture of the two gases in the tubes occurs; in 1905 a terrific explosion occurred at the Milan foundry, and killed and wounded a number of people.

The Garuti batteries were at first made entirely of lead, and the electrolyte consisted of water acidified with sulphuric acid. They now consist of a rectangular iron box, *N* (Fig. 42), divided by iron sheets about 1 mm. thick (the diaphragms), coated on both faces with metallic gauze, to facilitate the separation of the small bubbles of gas produced by the current from the ions. There are thus several cells, closed at the top and at the sides (*see* Figure *below*), but communicating below through small holes in the diaphragms, these permitting circulation of the electrolyte. In these cells positive and negative electrodes, consisting of iron plates about 1 mm. thick (the anodes last two to three years, the cathodes much longer), of rectangular shape with a small extension alternately in the one direction or the other (*B* and *C*), are introduced alternately in such a manner as to enable all the positive poles on one side of the box (voltameter) and all the negative poles at the other side to be connected.

The walls of each cell are about 20 mm. apart, and between each diaphragm (wall) and the interposed electrode the distance is about 10 mm., so that the resistance is small; in order to prevent the thin electrodes from bending and coming into contact with the diaphragms they are wrapped round at intervals with an asbestos cord, *t*, which keeps them in position.

The cells containing the cathodes (*b*) develop hydrogen, which passes off through an opening at the top; the neighbouring cells, containing the anode, *a*, develop oxygen, which also passes off through an orifice above. A pyramidal chamber, placed above the battery, collects all the oxygen, and another similar chamber all the hydrogen (*see* Fig. 43). By means of two tubes made of insulating material, such as glass, porcelain, or rubber, these two chambers communicate with gasometers. Each of these chambers contains a fair quantity of mother-liquor.

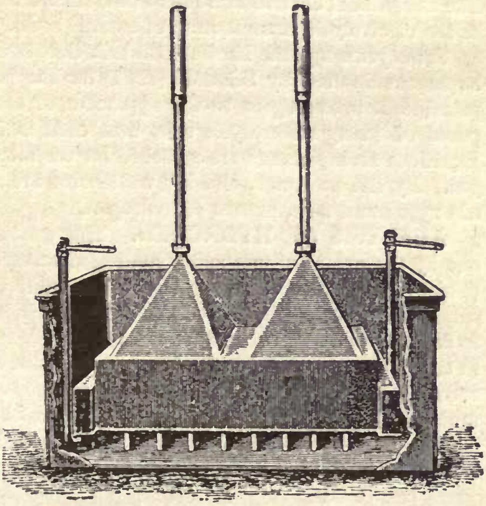


FIG. 43.

The electrolyte consists of a 26 per cent. aqueous solution of sodium hydroxide, which remains unaltered practically indefinitely if the water is replaced gradually as the electrolysis proceeds.

The caustic soda must be very pure, as otherwise the electrodes are corroded owing to the presence of chlorides and sulphates, which form Cl and SO_4 ions and attack the metal. These iron batteries are welded autogenously throughout with the oxy-hydrogen blow-pipe; they are stronger than the original leaden batteries, and certain solders are avoided which acted as voltaic couples and produced detonating gas. The lead batteries also polarise more easily. The caustic soda solution has now been replaced by a solution of caustic potash of 31° Bé., because this offers less resistance to the current and thus saves electrical energy.

In an apparatus thus constructed an E.M.F. of 2 volts is sufficient for a current of 2 amps. per sq. decimetre of electrode at a temperature of 30°.[1]

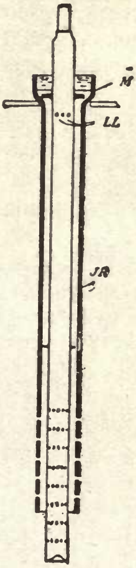


FIG. 44.

---

[1] The iron batteries are constructed with capacities of 200, 400, and even 3200 ampères, and always for an E.M.F. of 2 to 2·8 volts. With cheap hydraulic power of 1000 h.p., 5000 cu. metres of gas ($O + H_2$) are obtained per day, at an inclusive cost of 0·5*d.* per cu. metre. In small plants 1 kw.-hour produces about 160 litres of hydrogen and 80 litres of oxygen.

An apparatus analogous to that of Garuti was also produced in France by Colonel Renard for military purposes, with iron electrodes, a bath of caustic soda, and diaphragms of asbestos. It was, however, less perfect than the Garuti battery and required double the amount of energy per volume of gas produced. The Société ossidrique française was first formed in Belgium and in 1901 in France, with a capital of £40,000, for the production of oxygen and hydrogen by the Garuti system.

In 1901 Schoop introduced a cheap and carefully planned apparatus for the electrolytic production of hydrogen on a large scale. The electrodes are of lead, in the form of tubes, and there are no diaphragms. The baths consist of water acidified with sulphuric acid. The apparatus is also constructed in iron with 15 per cent. caustic soda as an electrolyte. The Schoop electrodes are very simple (Fig. 44). There are two long concentric lead cylinders of which the outer serves as a collecting tube, and more or less as a diaphragm, whilst the inner

A method not very different from that of Garuti, but with non-porous diaphragms of ebonite, has been proposed and applied at Hanau since 1897 by the electrical firm of Schuckert & Co., and appears to be successful.[1]

At the Elektron Works at Griesheim-on-Rhine hydrogen is prepared by the electrolysis of potassium chloride : $2KCl = K_2 + Cl_2$ and then $K_2 + 2H_2O = 2KOH + H_2$. By this reaction three important products, chlorine, hydrogen, and caustic potash, are obtained. The Società del Caffaro at Brescia now makes use of the hydrogen evolved at the cathode in the electrolytic manufacture of caustic soda.

Some years ago the Maschinenfabrik Oerlikon (Switzerland) constructed an electrolytic apparatus devised by Schmidt (1902) for the manufacture of hydrogen and oxygen; in principle it is analogous to the apparatus of Garuti, but occupies less space, being composed of many electrolytic cells combined and connected together as in a filter-press. Ingenious arrangements are attached for the almost automatic control of the purity of the gas. By this process twelve kilowatt-hours are required for the production of 1 cu. metre of oxygen and 2 cu. metres of hydrogen.

ANALYSIS OF HYDROGEN. The qualitative detection of impurities is carried out by the ordinary methods; hydrogen arsenide is detected with the Marsh apparatus (which also permits of its quantitative determination; *see* Hydrogen arsenide) and hydrogen sulphide by immersing paper impregnated with lead acetate for some time in the hydrogen to be analysed. The quantitative analysis also follows the ordinary methods of gas analysis in an Orsat apparatus (*see* Carbon and Analysis of Furnace Gas); by determination of the successively absorbed volumes the percentages of CO_2, O, and CO are found; that which remains is hydrogen, which may contain admixed nitrogen. This is passed through a hot capillary tube containing a thread of palladinised asbestos which absorbs all the hydrogen, leaving the nitrogen. Temperature and pressure must be allowed for in measuring the gases (*see* p. 26).

---

tube is the true electrode, and is supported by means of an insulating disc, *M*, in the wider neck of the outer tube, which forms a hydraulic seal. The inner tube is perforated at the base and near the top (*LL*), so that the gas which is formed may enter the inside of this tube and thus be conducted to the gasometer.

The cylindrical electrodes are introduced in large number into a tall vessel containing the electrolyte, which is pure sulphuric acid of sp. gr. 1·23. All the negative electrodes, forming hydrogen, are connected with a single collecting tube, and all the oxygen anodes with another. A plant on Schoop's system is worked at the accumulator factory of G. Hagen, at Kalk, near Cologne, with a current of 200 amps. at 65 volts. Schoop calculates that the gas produced costs about 3·7*d.* per cubic metre.

[1] For a small installation with a daily production of 100 cu. metres of oxygen and 200 cu. metres of hydrogen, the cost of plant and working expenses would be as follows :

	£
40 voltameters for 600 amps.	500
Pipe system, alkaline bath, installation, etc.	200
Roofed building of 70 sq. metres area	200
Total cost of plant	900

The daily cost of working—using a waterfall supplying a kilowatt-year at a cost of £7 10*s.* (using steam power the kilowatt-year would cost about £20)—are as follows :

	£	*s.*	*d.*
Daily cost per 60 kilowatts	1	12	9
Consumption of electrodes and electrolyte		3	7
Various repairs to machinery and buildings		4	3
Wages of two workmen		8	0
Sinking fund, 15 per cent. on £900		9	7
Sundry expenses		2	10
Total daily expenses	3	1	0

Thus each cubic metre of gas (H and O) costs 2·5*d.* If this gas is to be sold, 2·5*d.* must be added for the cost of compression in steel cylinders.

It will be clear that where energy is much cheaper than is assumed above, the cost of producing the gas will also be much less.

(*Translator's note.*—In England a kilowatt-year, produced by steam, costs much less than £20.)

(A) NON-METALS; HALOGEN GROUP

This is the first group of non-metals and consists of four monovalent elements, fluorine, chlorine, bromine, and iodine :

$$F = 19; \ Cl = 35{\cdot}46; \ Br = 79{\cdot}92; \ I = 126{\cdot}92.$$

They are called *halogens*, from a Greek word meaning salt-formers, and in fact, they combine easily and directly with almost all metals and with bases to form salts.

In their physical properties they vary gradually with increasing atomic weight, with which the density also increases, and they pass from the gaseous to the solid state :

	F	Cl	Br	I
Atomic weight	19	35·46	79·92	126·92
Melting-point	−252°	−101·7°	−7·2°	+ 114°
Boiling-point	−187°	−33·7°	+ 60°	+ 184°
Specific gravity in the liquid state	1·108	1·47	3·18	(as solid) 4·9
Colour	pale yellowish	yellowish green	brown	blackish violet

The affinity of these elements for metals and hydrogen is large in the case of F and Cl, and decreases in the direction of iodine, that is, with increase of atomic weight. As the affinity decreases in this way it is possible in many compounds to substitute or displace iodine by bromine, bromine by chlorine, and chlorine by fluorine. In the combinations with oxygen the affinities increase in the reverse direction, that is, the oxygen compounds of iodine are more stable than those of chlorine, and fluorine does not combine with oxygen at all.

Minimal traces of the halogens facilitate and often cause chemical reactions which do not take place under ordinary conditions (Schuyten, 1907–1909).

FLUORINE : F, 19

This element has only been known in the free state since 1886. Before that time it was known solely in the combined state, and therefore its properties were only indirectly utilised by means of its more important compounds (fluorspar or fluorite, CaF_2; cryolite, AlF_3, 3NaF, etc.). The addition of fluorspar to minerals to facilitate their fusion was already known to Basil Valentine in the fifteenth, and to Agricola in the sixteenth century, and was practised in those times. The luminosity of fluorspar when heated is recorded in various writings in 1667. Moissan stated that he had recognised free fluorine in the gaseous occlusions in a fluorspar from Quincié.

It is also found in small quantity combined as calcium fluoride in the bones of man and other mammals, and in the enamel of the teeth; fluorine must therefore pass into the blood in some form, and is provided by certain human foods (milk and vegetables).

PROPERTIES. It is a slightly greenish yellow gas, with an odour similar to that of hypochlorous acid. It has no absorption spectrum and is completely non-magnetic. The red part of its luminous spectrum (emission spectrum) is composed of thirteen characteristic lines.

Fluorine is ordinarily considered to be monovalent, but Blomstrand (1869), on account of the existence of acid fluorides, and Thomsen, for the same reason, and also from the heat developed on saturating silicic acid with hydrofluoric acid, consider fluorine to be divalent and hydrofluoric acid to have the constitution H — F — F — H. Further work is required to clear up this question, but we now know fluorides of silver and of calcium, Ag_2F and CaF.

Fluorine combines even in the dark with H, I, S, Si, Se, B, As, Sb, Fe, Mn, with all organic compounds, etc. The metals are strongly attacked with the exception of gold and platinum. It attacks water, forming HF and ozonised oxygen (O_3). It displaces Cl, Br, and I from their metallic compounds. It only combines with carbon at a red heat, and does not combine with diamond under these conditions. Cork is immediately carbonised by it. This great reactivity is the cause of the great difficulty encountered in liberating the free element, and gives ground for hope that important applications await this interesting element in the future.

In 1897 Moissan and J. Dewar succeeded in liquefying fluorine at —187° (with boiling liquid oxygen), but it did not solidify at — 210°. At this temperature it loses almost completely its extraordinary chemical affinity for many substances, and no longer reacts with water, mercury, etc., but still reacts with hydrogen, and ignites benzene and oil of turpentine. When perfectly dry it does not attack well-dried polished glass. The liquid is of yellow colour and has a specific gravity of 1·108 at —187°, that is, at the boiling-point (Ramsay, 1900). In 1903 it was solidified by Moissan and J. Dewar by means of liquid hydrogen at — 252°, and then formed a white mass, exploding violently in contact with liquid hydrogen; it melts at — 223°.

PREPARATION. It was known as early as 1670 that when fluorspar is mixed with oil of vitriol (H_2SO_4) it attacked glass, and in 1781 Scheele obtained free hydrofluoric acid, which he prepared in vessels of lead or fluorite, as he knew that it attacked glass and almost all metallic vessels. In 1810 Ampère showed that this acid is a hydrogen compound.

The attempts to obtain free fluorine were very numerous and were prosecuted by many able chemists of the past century. From Davy (1818) to the brothers Knox (1841), Louyet (1847), Kammerer (1865), Finkener (1867), Fremy, etc., there was a continuous series of abortive experiments. When they thought they had obtained fluorine the gas was quickly shown to be either hydrofluoric acid or oxygen. The action was tried, without success, of chlorine and iodine on the fluorides of silver and of mercury, at high temperatures (Davy) in tubes of glass and of platinum and in vessels made of fluorspar. The same negative result was obtained by the electrolysis of dry hydrofluoric acid with a positive electrode of carbon.

All this proved useless, and even if free fluorine could be formed in such reactions a minimal trace of moisture sufficed to cause it to enter into combination, even with the substances composing the vessels in which it was prepared.

Moissan succeeded only in 1886 in finally obtaining free fluorine with certainty, by employing many precautions to prevent it from combining with other substances. He started from absolutely anhydrous hydrofluoric acid, obtained by heating potassium hydrogen fluoride, HF, KF, and collecting this in a platinum U-tube connected with a delivery tube of platinum and closed by cocks of fluorspar.

The negative electrode, at which liberation of the hydrogen was expected, was made of pure platinum, and the positive electrode, where the fluorine was to be liberated, was made of an alloy of 90 per cent. platinum and 10 per cent. iridium. The apparatus was cooled to —23°, and, when connected with a battery of twenty Bunsen cells producing a current of 20 amps., this did not pass through the hydrofluoric acid in the apparatus. The addition of a minimal trace of moisture, however, quickly allowed the current to pass, but free fluorine was not then obtained. Thus this attempt to prepare fluorine electrolytically failed, equally with those of other chemists. Moissan finally succeeded in rendering dry hydrofluoric acid electrically conductive by the addition of a small quantity of dry potassium hydrogen fluoride. At the positive pole a gas was then obtained which proved to be real fluorine.

Moissan also prepared this gas by direct electrolysis of fused dry potassium hydrogen fluoride, replacing the platinum by copper vessels.

In 1900 Poulenc and Meslan prepared considerable quantities of fluorine electrolytically in a copper apparatus, which very soon became covered with copper fluoride and then became unattackable; the anodes and cathodes were of copper and were insulated with rubber. The whole apparatus was cooled during the electrolytic decomposition.

A small apparatus for laboratory use is shown in Fig. 45. A small copper box, *B*, supported by the lid, *M*, carries on its inner walls sheets of copper, *G*, which serve as cathodes. The copper tube, *A*, perforated near the base, *d*, forms the chamber which contains the platinum anode, *p*, which is cooled by the liquid which circulates in the tube *T*. Fluorine escapes by the tube *R*, and hydrogen by the tube *H*. The box, *S*, contains a freezing mixture.

The electrolyte consists of a very cold solution of potassium fluoride in anhydrous hydrofluoric acid. G. Gallo (1910) did not obtain good results with the apparatus of Poulenc and Meslan, and replaced it with advantage by a smaller and simpler apparatus of platinum; this consisted of an ordinary platinum crucible which was attached to a metallic ring serving to connect it with the negative pole of the electric battery. The crucible was closed with a gas-tight lid of sulphur, which is a very excellent material for such work on account of its easy fusibility and its strong adherence to many metals. Through the centre of the sulphur plug was fixed a small cylinder of platinum which ended inside the crucible without touching it, and which acted as a diaphragm. The small cylinder is easily made by rolling a sheet of platinum foil on to itself and twisting up the ends. It is closed below by a platinum disc and is pierced with lateral holes at the base. Inside it is fixed a fairly thick platinum wire which serves as the positive pole and terminates outside the sulphur plug. The fluorine evolved inside the crucible does not come into contact with the sulphur, as this is protected by a disc of potassium fluoride.

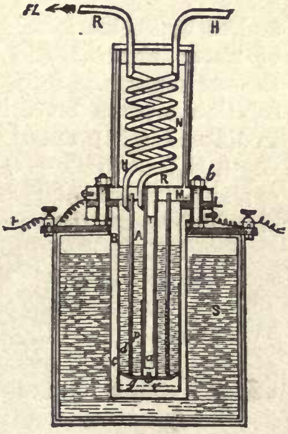


FIG. 45.

The inside of the crucible communicates with the outside by means of two spiral copper tubes passing through the sulphur plug, one entering the anodic and the other the cathodic space. These serve as delivery tubes for the fluorine and hydrogen respectively. The two spirals are contained in a copper sleeve filled with a freezing mixture. The anhydrous hydrofluoric acid and potassium hydrogen fluoride are introduced through a hole in the sulphur lid, this being then closed with a plug of sulphur which may be fixed by fusion.

During electrolysis the crucible is immersed in methyl chloride which boils at − 23°, and under these circumstances free fluorine is obtained by employing a current of 2 to 3 amps. at 50 volts.

CHLORINE : Cl, 35·46

Chlorine is a gas which was discovered by Scheele in 1774, but is never found free in nature on account of its great chemical activity. It is found very abundantly, however, in the form of chlorides such as rock salt and sea salt ($NaCl$), sylvine (KCl), carnallite ($KCl, MgCl_2 + 6$ aq.), etc. It is found in combination in small quantities in all vegetables, in blood, animal secretions, etc.

PHYSICAL PROPERTIES. Chlorine is a yellowish green gas of suffocating odour, with a density of 2·45 compared with that of air.

One litre of chlorine weighs 3·167 grms.; it is liquefied at 15° under a pressure of 5·7 atmospheres or at − 40° at the ordinary pressure, forming a dark yellow liquid (sp. gr. 1·557), which boils at − 33·6° and forms a yellow crystalline solid at − 202° (*see* p. 157, Liquid Chlorine) The vapour density at 1200° was found by V. Meyer to be less than that corresponding with the molecular weight, and he assumed that some of the Cl_2 molecules had undergone dissociation; it seems, however, from later experiments that it is a case rather of exceptional behaviour of this gas with respect to the laws of Boyle and Gay-Lussac, and that the density increases by more than the amount calculated from these two laws when the pressure is increased or the temperature diminished; it has been recently shown that even at 1137° there is no appreciable dissociation.

Wood charcoal absorbs as much as 200 vols. of chlorine with evolution of 6780 calories for each 35·5 grms. of chlorine absorbed. This chlorine is liberated when the charcoal is heated.

At 90° water absorbs extremely little chlorine; at 20° 1 vol. of water absorbs 2 vols., and at 10° $2\frac{1}{2}$ vols.; chlorine water is thus obtained, the properties of which are almost the same as those of chlorine, though it seems that in solution a state of equilibrium is produced according to the following equation:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO,$$

and as hydrochloric acid is dissociated there will be in the solution a mixture of water, chlorine, and hydrochloric and hypochlorous acids, together with the corresponding ions. Under the action of light all the chlorine in the solution is transformed into HCl (in four days in direct, and in thirty-six days in diffused light), passing through the stages of hypochlorous and chloric acids: $Cl_2 + H_2O = 2HCl + O$ (Ferentzy, 1908), from which we are also able to explain the oxidising power of chlorine water. At temperatures below 0° chlorine water deposits crystals of chlorine hydrate ($Cl,8H_2O$).

CHEMICAL PROPERTIES. In certain compounds chlorine is no longer monovalent, but polyvalent, *e. g.*, in ClO_2, etc. Chlorine combines directly with all the elements except nitrogen, oxygen, and the new gases, argon, helium, etc. The chlorine ions, Cl', of soluble chlorides combine readily with the silver ions of silver nitrate, forming a characteristic flocculent white precipitate of silver chloride, soluble in ammonia.

The great reactive power of chlorine may be shown by various simple experiments. A piece of phosphorus immersed in a flask of chlorine first melts and then catches fire spontaneously, giving out a bright light and producing white fumes which deposit as a white powder of phosphorus pentachloride, PCl_5.

Powdered antimony, when thrown into a jar of chlorine, immediately catches fire, and thin foil composed of other metals, such as pinchbeck, tin, etc., behaves in a similar manner. These materials do not, however, react with liquid chlorine at − 90°.

Hydrogen and chlorine combine with detonation when a flame is brought in contact with the mixture; bright daylight is also able to bring about the explosion, especially if the mixture is moist and freshly prepared electrolytically from HCl. The combination proceeds more slowly in diffused light and still more slowly in the dark. The heat of combination of H and Cl is about 92 Kj. (22,000 cals.). A *dry* mixture of H and Cl does not react in the dark, even in fifteen months; at − 25° the mixture does not explode even under the action of intense light.

Chlorine combines also with hydrogen present in combination, for example, with the hydrogen of many organic compounds, and also with that in water, yielding oxygen. Thus, a piece of paper soaked in turpentine (which is an organic compound containing carbon and hydrogen) burns rapidly with formation of carbon when introduced into a cylinder of chlorine.

Chlorine has a decolorising action on many coloured organic substances, both natural and artificial; it easily bleaches solutions of soluble indigo, logwood, and litmus, fresh flowers, many artificial flowers, etc. Fabrics dyed with various aniline dyestuffs are not bleached by chlorine when dry, but are rapidly bleached in presence of moisture.

Chlorine does not burn in the air, but it burns in an atmosphere of hydrogen, so that it is a combustible substance. The property of a substance of being combustible or a supporter of combustion is, however, relative to the conditions under which the reaction takes place; thus, for example, chlorine is also a supporter of combustion, for a flame of hydrogen or coal-gas, or a burning candle continues to burn in a cylinder of chlorine, the hydrogen burning with a blue flame and the coal-gas and the candle with a sooty flame, as chlorine removes hydrogen from organic compounds with separation of carbon. In all these cases hydrochloric acid is formed and can be recognised by its action on litmus paper.

Chlorine displaces iodine from iodides and bromine from bromides because the heat of formation of chlorides is greater than those of the corresponding bromides and iodides (third law of thermochemistry):

$$KI + Cl = KCl + I + 25{,}500 \text{ cals.}$$

Chlorine also reacts incompletely with steam in presence of heated carbon to form hydrochloric acid: $2Cl + 2H_2O + C = 4HCl + CO_2$ (Lorenz, 1895 and 1897).

In spite of being a supporter of combustion and an oxidising agent chlorine is irrespirable and is quite unable to replace oxygen in our organism.

When inhaled, even in small quantity, it attacks the lungs, causing coughing and spitting of blood. It does not act as a poison on the heart, but paralyses the respiratory centres. Its action on animals is already perceptible when mixed with air in the proportion of 1 c.c. per cubic metre. Air containing one-millionth part of chlorine is harmful to man. The smoking of tobacco, inhalation of steam, or the vapours of alcohol or aniline, and also of air containing a little hydrogen sulphide are all found to be of benefit in counteracting the effects of chlorine on the system.

It is an energetic disinfectant and is used in cases of epidemics in the form of a solution of chloride of lime for purifying floors, walls of living-rooms, stables, cesspools, etc.

APPLICATIONS OF CHLORINE, PRICES, AND STATISTICS. In order to be able to make use of chlorine it is necessary to obtain it in a convenient form for handling, either as compressed or liquefied gas in cylinders, or as a solid in the form of *chloride of lime.* The preparation of the latter is described in Part III (Hypochlorites).

Chlorine is used industrially for bleaching vegetable textiles, cotton, paper, etc., and for preparing wool for printing, because when the wool is gently oxidised the dyestuffs are more firmly fixed. It is also used for the preparation of hypochlorites, of chlorinated organic compounds, such as chloroform, chloral, etc., and also for the preparation of carbon tetrachloride, which has now acquired great industrial importance (*see also* Uses of Chloride of Lime).

Liquid chlorine is used in large quantity at Stassfurt for the preparation of 500,000 kilos of bromine annually, and the Badische Anilin und Soda Fabrik at Ludwigshafen in 1900 used more than a million kilos for the production of chloracetic acid, which is used in the synthetic preparation of *artificial indigo.* For the manufacture of aniline dyestuffs, 10,000,000 litres of liquid chlorine are used per annum. In Italy 75,000 kilos of liquid chlorine were produced in 1907 and almost 200,000 kilos in 1909, sold in steel bombs holding 60 kilos at £2 12*s.* per 100 kilos; in 1911 the production was 184,000 kilos.

The problem of the utilisation of chlorine has become very urgent because the electrolytic soda-works produce it in quantities very much larger than the demand, and whereas in the past hydrochloric acid has been used as a source of chlorine, convenient methods of conversion of chlorine into hydrochloric acid are now being sought for (*see* Hydrochloric Acid).[1]

The commercial price of compressed chlorine in steel bombs, holding from 5 to 50 kilos, is about 6*d.* to 1*s.* 2*d.* per kilo; the empty bomb costs £1 8*s.* for a capacity of 5 kilos of chlorine, and £2 16*s.* for a capacity of 50 kilos; the bombs are, however, lent on hire by the manufacturers. Saturated chlorine water is sold at 12*s.* per 100 kilos, including carboys.

For the cost of manufacture of electrolytic chlorine, *see* Part III, Electrolytic Soda.

LABORATORY PREPARATION OF CHLORINE. Chlorine was first prepared by Scheele in 1774, by acting on manganese dioxide with hydrochloric acid, but nothing was known as to its nature, so that in 1775 Berthollet declared it to be oxidised hydrochloric acid. Davy first demonstrated in 1810 that chlorine was a simple substance on the ground of its behaviour with red-hot carbon (in contact with which it remained unaltered), and also by showing that when certain metallic oxides are heated in a current of chlorine, oxygen alone is evolved in quantity corresponding with the amount of chlorine fixed by the metal; thus chlorine was shown to contain neither oxygen nor hydrogen. For a long time, however (until 1820), Berzelius and Schönbein still regarded chlorine as an oxidised compound of hydrochloric acid.

It is now prepared by the action of hydrochloric acid on substances which readily give up oxygen, this combining with the hydrogen of the hydrochloric acid, liberating the chlorine. As oxidising compounds one may use the oxides of manganese, chromic acid, nitric acid, sodium chlorate, etc.

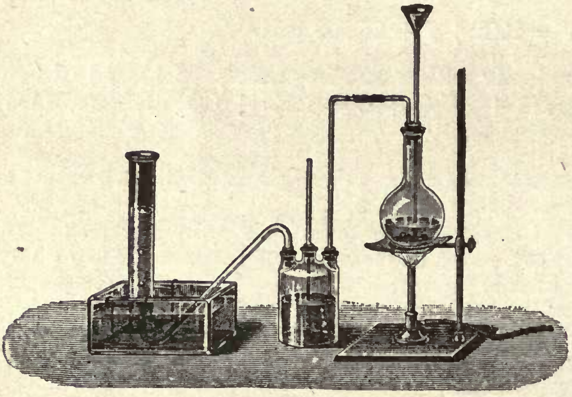


Fig. 46.

It is ordinarily prepared in the laboratory by heating manganese dioxide with hydrochloric acid: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. Chlorine is not developed in the cold, as a soluble tetrachloride of manganese is formed: $MnO_2 + 4HCl = MnCl_4 + 2H_2O$; on heating, the reaction $MnCl_4 = MnCl_2 + Cl_2$ takes place.

In the laboratory a mixture proposed by Klason is often preferred, as a more regular evolution of chlorine is so obtained on heating on the water-bath; it consists of 5 parts of MnO_2 (of 90 per cent. strength), 11 parts of NaCl, 14 parts by weight of strong sulphuric acid, and 7·5 parts by weight of water (equal in volume to the sulphuric acid):

$$4NaCl + MnO_2 + 3H_2SO_4 =$$
$$2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O + Cl_2.$$

In this manner 95 per cent. of the quantity of chlorine indicated by the equation is obtained in practice. The laboratory apparatus is illustrated in Fig. 46; the chlorine is washed in hot water in a Woulff's bottle, and then collected in a cylinder inverted over a pan of hot water, as chlorine is somewhat soluble in cold water.

---

[1] This refers to normal times, as during the war enormous amounts of chlorine were required for making asphyxiating gas (chlorine, phosgene, or chlorinated organic compounds), for preparing immense quantities of chlorobenzene for producing dinitrophenol (which, mixed with picric acid, forms a powerful explosive), for making sulphur blacks for the direct dyeing of cotton, etc. During the war the price of compressed chlorine reached and even exceeded 1*s.* 7*d.* per kilo, and Europe imported large quantities from America in large steel bombs, each holding 150 kilos.

In 1901 Graebe obtained chlorine by heating a solution of sodium chlorate with hydrochloric acid, but a little chlorine oxide, ClO_2, is also formed; this may, however, be decomposed by passing through a red-hot tube. In 1903 he made it by the action of cold hydrochloric acid (density 1·16) on solid potassium permanganate, and so obtained pure chlorine free from oxides.

Relatively pure chlorine is obtained by heating potassium dichromate (100 grms.) with hydrochloric acid in a flask of about 200 c.c. capacity and collecting over hot water without washing:

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 3Cl_2 + 7H_2O.$$

Another rapid laboratory method, suggested by Winkler, consists in acting in the cold in a Kipp apparatus with hydrochloric acid on small cubes made from four parts of chloride of lime ($CaOCl_2$) mixed to a paste with one part of plaster of Paris:

$$CaOCl_2 + 2HCl = CaCl_2 + Cl_2 + H_2O.$$

Small traces of oxygen are also formed by this method.

By decomposing dilute hydrochloric acid with the electric current chlorine is obtained at the anode and hydrogen at the cathode, and in the same way concentrated solutions of sodium chloride give chlorine at the anode and caustic soda and hydrogen at the cathode as secondary products formed by the action of water on the sodium which is separated as the primary product: $Na + H_2O = NaOH + H$.

According to Ferentzy (1908) it is impossible to obtain absolutely pure chlorine by any of the above-mentioned methods, as it always contains chlorine oxides, the presence of which was proved by diffusion through tubes of porous porcelain heated to 1200°, the oxygen from the chlorine oxides passing through their walls. Chemically pure chlorine can only be obtained by decomposing potassium platinichloride at a red heat: $K_2PtCl_6 = 2KCl + Pt + Cl_4$.

INDUSTRIAL METHODS OF PREPARING CHLORINE. Until a few years ago the industrial preparation of chlorine was almost entirely confined to purely chemical processes; to-day, on the contrary, almost the whole supply is produced as an abundant (too abundant) by-product of the electrolytic production of caustic soda and potash. For this reason we shall here only discuss briefly the chemical methods still in use, and in Part III, in describing the electrolytic soda industry, we shall consider also the preparation of chlorine and chloride of lime.

I. In small industrial installations chlorine is readily obtained by the action of hydrochloric acid on natural manganese dioxide (pyrolusite, polianite, manganite, etc.), which is found in deposits in Germany, Spain, and South America, in moderate quantity in Piedmont and in abundance in Eubaea. The value of this mineral is proportional to the quantity of manganese dioxide, MnO_2, which it contains, as the other oxides, MnO, Mn_3O_4, and Mn_2O_3, are less valuable and yield less chlorine and more manganese chloride, thus using more hydrochloric acid:[1]

$$MnO_2 + 4HCl = 2H_2O + MnCl + Cl_2$$
$$Mn_3O_4 + 8HCl = 4H_2O + 3MnCl_2 + Cl_2.$$

---

[1] *Analysis of pyrolusite.*—In addition to determinations of the moisture and the carbonates, the percentage of MnO_2 is determined as follows: 1·0875 grms. of dry powdered pyrolusite are placed in a stoppered flask fitted with a Bunsen valve and 75 c.c. of a ferrous sulphate solution (prepared by dissolving 100 grms. of pure ferrous sulphate and 100 c.c. of sulphuric acid in water to 1 litre), which has been previously titrated with a $\frac{1}{2}$-N solution of potassium permanganate then added. The contents of the flask are boiled for some time, the valve permitting the steam to escape whilst preventing the entry of air. The whole is then cooled and the contents of the flask titrated with $\frac{1}{2}$-N permanganate; if the amount of permanganate required for this purpose is subtracted from the amount corresponding with 75 c.c. of the ferrous sulphate solution, the amount corresponding with the MnO_2 in the sample is found; on multiplying this number of c.c. by two, the percentage of MnO_2 is found (1 c.c. of $\frac{1}{2}$-N permanganate = 0·02175 grm. MnO_2).

In order to obtain the same quantity of chlorine from Mn_3O_4 double the quantity of hydrochloric acid is required. A mineral containing less than 57 per cent. of MnO_2 is unsuitable for the purpose, as is also the case if it contains more than 1 per cent. of CO_2 as carbonate. The higher oxides are valued commercially according to the amount of MnO_2 they are capable of yielding:

$$Mn_2O_3 = MnO + MnO_2 \quad \text{or} \quad Mn_3O_4 = 2\,MnO + MnO_2.$$

The industrial preparation of chlorine is carried out in vessels of cast-iron or earthenware containing HCl and MnO_2. These are heated with hot water or steam, and when the reaction has finished, the mother-liquors, which contain $MnCl_2$, are removed by syphons and used for the regeneration of chlorine and manganese dioxide. The delivery tubes for the chlorine are constructed of lead or earthenware. The heating operation lasts twenty-four hours altogether. Lunge advises the apparatus illustrated in Fig. 47. A stoneware cylinder, *a*, with a perforated double bottom, *b*, contains the manganese dioxide and hydrochloric acid. This cylinder is closed by a bell, *d*, immersed in a large cylinder, *h*, containing water heated by the steam-pipe, *i*. The regular stream of chlorine thus produced escapes by the tube *g*. The mother-liquor containing manganous chloride is discharged by the tube *c*, and the manganese recovered by one means or another.[1]

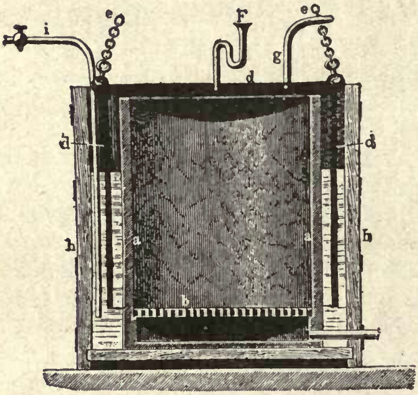


FIG. 47.

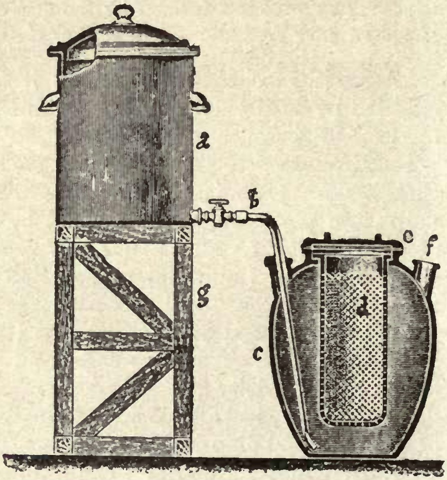


FIG. 48.

The apparatus constructed entirely in stoneware and shown in Fig. 48 is simpler and more commonly used. The vessel, *c*, contains manganese dioxide

---

[1] *Treatment of the mother-liquor.*—This contains $MnCl_2$ and the excess of HCl (5 to 6 per cent.); it is treated in various ways to recover manganese dioxide.

(A) *Dunlop's method.*—The liquor is heated at four atmospheres pressure with calcium carbonate: $MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2$. The manganese carbonate thus formed is then heated in furnaces at 300° in presence of air and forms manganese dioxide: $MnCO_3 + O = CO_2 + MnO_2$. This method is employed only in Tennant's works.

(B) *Weldon's methods.*—(*a*) *With lime.* In 1837 Gossage proposed to treat the mother-liquor ($MnCl_2$ and HCl) with lime and then to oxidise the mass with air: $2MnCl_2 + 3CaO + O_2 = 2CaCl_2 + CaO, 2MnO_2$.

In 1860 Binks and Macqueen patented this process, but the credit of its successful application in practice and of demonstrating the importance of an excess of lime is due to Weldon. Calcium chloride is soluble and is thus separated from the sludge, which is then returned to the chlorine generators.

(*b*) *With magnesia.*—The mother-liquor ($MnCl_2$ and HCl) is neutralised with magnesium carbonate, and then contains a mixture of $MgCl_2$ and $MnCl_2$. The whole is evaporated and dried in furnaces until HCl commences to be evolved. It is then placed in retorts and regularly heated in a current of air; chlorine is thus developed and can be utilised: $MnCl_2 + O = MnO + Cl_2$, and also $MgCl_2 + O = MgO + Cl_2$. The mixture of the two oxides is again employed in the chlorine generators. On account of many technical difficulties and in spite of various improvements the magnesia method has never found technical application.

in the internal perforated cylinder, *d*, this reacting with the hydrochloric acid which enters from the reservoir, *a*, through the tube, *b*. The chlorine escapes through *f*, and is developed regularly and completely if the vessel, *c*, is immersed in a vat (not shown in the figure) containing water heated by a steam-jet. The apparatus is completely closed by the heavy cover, *e*.

II. **CHLORINE FROM AIR AND HYDROCHLORIC ACID.** *Deacon-Hurter method*, 1870. This is based on the action of air (oxygen) on hydrochloric acid when heated in presence of an active substance which acts by contact alone (catalytically) or forms an intermediate product which is easily decomposed, continuously producing chlorine. As active material small clay balls impregnated with copper chloride or sulphate have been found to work well. It has, however, been shown that other substances, even inert materials, such as moist pumice stone, are able to produce the same catalytic effect.

On heating copper chloride, $CuCl_2$, under these conditions, it undergoes the decomposition: $2CuCl_2 = Cl_2 + Cu_2Cl_2$ (cuprous chloride), the latter being reconverted into cupric chloride by hydrochloric acid and the oxygen of the air: $Cu_2Cl_2 + 2HCl + O = H_2O + 2CuCl_2$.

Thus $CuCl_2$ plays a part in the reaction, but is continually regenerated, so that the process may be represented by the equation:

$$2HCl + O = H_2O + Cl_2.$$

In practice many difficulties are encountered: the $CuCl_2$ is not completely regenerated, the HCl is not completely converted into chlorine, and the catalytic action of the copper salt becomes exhausted after a short time, on account of the impurities which accumulate in it. The best results are obtained when the following precautions are observed:

The temperature should not exceed 470°, otherwise cuprous chloride is volatilised and lost.

The yield of chlorine depends greatly on the proportions in which HCl and air are present, and on the velocity of the current of these gases. The best results are obtained when the reacting gaseous mixture contains 15 to 20 per cent. of HCl, and the emerging stream of gas after the reaction contains 5 to 7 per cent. of chlorine, the rest being air. When a mixture of 40 per cent. HCl and 60 per cent. air is used, 70 per cent. of the HCl is converted into chlorine. The presence of sulphuric acid or SO_2, derived from the furnaces which produce the HCl, reduces the yield of chlorine, owing to the following reaction:

$$SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$$

(*see below*, Hydrochloric Acid).

The process was improved by Lunge and by Solvay about 1890; they endeavoured to eliminate all the above difficulties, and were able to introduce their improvements into many large plants. Still until 1902 a notable loss of $CuCl_2$ was observed (about 50 per cent. in ten days) and Dieffenbach therefore arranged the plant in such a manner as to regenerate all the copper salt by forcing the gas to issue at a point of the catalytic mass where the reaction is less energetic and the temperature lower, thus avoiding volatilisation of the copper salt, and finally (1908) he diminished the volatility of the cuprous chloride by mixing it with sodium chloride (German patent No. 197,955).

The Deacon process is now advantageously employed wherever chlorine of a low degree of concentration is needed.

The arrangement of the plant is shown in longitudinal section in Fig. 49. To the left is seen the muffle-furnace for producing hydrogen chloride, which, mixed with air, is cooled and freed from the greater part of the accompanying moisture by passing through the long pipe, *a*. The gaseous mixture is well dried in the coke-tower, *b*, and then passes through a series of twenty-four pipes contained in a furnace, *c*, at a temperature of 450° to 470°; it then enters the reaction chamber, *d*, consisting of a large cast-iron cylinder maintained at 450° by hot fumes from the furnace, *c*, and divided into six compartments filled with fragments of porous brick impregnated with copper chloride or sulphate. After the reaction is completed the gases, consisting of chlorine, excess of hydrochloric acid, oxygen and nitrogen from the air, and steam, are cooled in several long tubes which condense the steam and hydrochloric acid. The last traces of HCl are separated in a coke-tower, from the top of which a fine shower of water descends, and the remaining gases are dried in a second coke-tower with a spray of strong sulphuric acid. Finally only dry chlorine mixed with air remains, the mixture containing 5 to 7 per cent. of chlorine.

III. CHLORINE FROM CHLORIDES. *Weldon-Pechiney Process* (1888–1890). This process can be conveniently used only where cheap magnesium chloride can be obtained, as at Neu Stassfurt ($MgCl_2 + O = MgO + Cl_2$).

The $MgCl_2$ solution is evaporated and made into a paste with dry magnesia. The hardened mass is broken up and the pieces thrown into a flue heated to 250° to 300° in which a current of hot air circulates. In this way almost all the water (65 per cent.) is evolved, but only 5 to 8 per cent. of the chlorine (as HCl). The perfectly dry magnesium chloride, mixed with MgO, is then introduced into a reverberatory furnace, consisting of high, narrow chambers, and heated to 1000°. The heating is continued for six hours, during which a regulated current of air is passed over the mass, causing the formation of chlorine, mixed with very little HCl. The latter is condensed in a suitable column, after which the gases contain about 8 per cent. of chlorine, but after five hours this percentage sinks to 1.

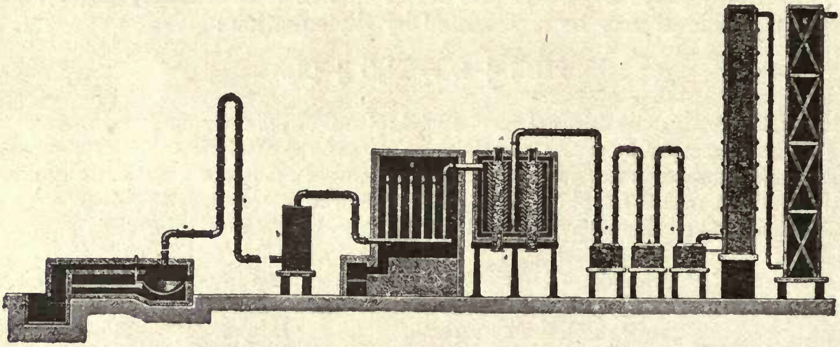


FIG. 49.

This process is in use, with trifling modifications, in many large works, and competes with the Deacon and electrolytic processes.

In order to utilise the calcium chloride obtained as a by-product in the manufacture of sodium carbonate Solvay proposed to heat it with silica to a high temperature in a current of air:

$$CaCl_2 + SiO_2 + O = CaSiO_3 + Cl_2.$$

This process has not yet succeeded in competing with the electrolytic process. The Dunlop process, modified by Goldschmidt, Davis, and Taylor, is also without technical interest, unless one is able to utilise the NOCl for the bleaching of flour. It is based on the reaction:

$$3HCl + HNO_3 = 2H_2O + Cl_2 + NOCl$$

and a yield of 82 per cent. of the chlorine is obtained. The same may be said of Schlösing's process (1862):

$$2HCl + 2HNO_3 + MnO_2 = Mn(NO_3)_2 + 2H_2O + Cl_2.$$

IV. ELECTROLYTIC METHODS OF CHLORINE MANUFACTURE. These are associated with the electrolytic manufacture of soda, and the various processes will, therefore, be discussed in detail in Part III, in the chapter on Electrolytic Soda.

However simple the electrolytic preparation of chlorine by decomposition of NaCl may appear, the technical difficulties encountered were so serious that industrial application of the process was long delayed.

The chlorine which is formed strongly attacks the metals of the plant and the carbon of the anode, while the caustic alkali quickly destroys many parts of the machinery. Parchment diaphragms were rapidly destroyed, and equally grave difficulties attended the use of every kind of diaphragm which was tried. Since 1890 there has been a bewildering succession of patents to embody the best arrangement of electrodes and diaphragms, or to eliminate the diaphragms altogether; to-day the problem may be said to be practically solved. The Elektron Company of Griesheim use anodes of magnetite (1914), in order that the chlorine may not contain an admixture of carbon dioxide.

The patents of Löwe and of Marx (Andreoli employed mercury as cathode, which was also adopted by Castner), of Hermite and Dubose, Kellner and Solvay, Hunt and Watson (1895), the Hargreaves-Bird process (1899), and that of Acker (1900) all indicated the progress of these determined attempts. In spite of the fact that its initiation required such great and very costly efforts the electrolytic process has to-day almost replaced all other processes of making chlorine.[1]

LIQUID CHLORINE. Liquid chlorine was first prepared in the laboratory by Faraday in 1823 and is to-day produced in large quantity for various industrial purposes, especially for the manufacture of bromine and iodine in the Stassfurt salt works.

Hannay prepared it industrially in 1890 by heating chlorine hydrate in a closed vessel of iron, lined with lead, separating the water which floats on the top, and conveying the liquid chlorine into a suitable steel cylinder with strong sulphuric acid, after drying.

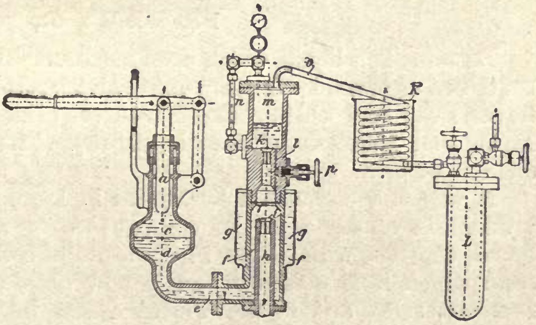


FIG. 50.

The Badische Anilin und Soda Fabrik, Ludwigshafen, compress electrolytic chlorine conveyed by the pipe, *h* (Fig. 50), over strong sulphuric acid in the iron receiver, *m*, and protect the piston, *a*, of the pump by separating it from the acid with a layer of pure petroleum, *c*. The gaseous chlorine, strongly compressed in this manner, and at a temperature of 50° to 80°, passes into a strongly cooled spiral condenser, *K*, where it is liquefied and collects in the steel cylinder, *L*. The valves, *i* and *k*, control the entry of the chlorine in accordance with the movements of the piston. The water-bath, *g*, is kept at 50° to 80°. Messrs. Schütze, Oggersheim, designed new forms of compressor for this process.

Chlorine is now liquefied without the use of a compression pump, as it is found preferable to liquefy it by strong refrigeration without compression; in either case, however, the chlorine should not be diluted with other gases to too great an extent.

When chlorine is mixed with other gases, as in the Deacon process, it is necessary to separate it before it can be liquefied, and Th. Goldschmidt therefore proposed (in 1907) to absorb it with a liquid chloride free from water, *e. g.*, anhydrous stannic chloride, at a pressure near its point of liquefaction. The dissolved chlorine is liberated on diminishing the pressure and, when necessary, heating.

Vessels to be used for the transport of liquid chlorine must be of iron or steel, and able to resist an internal pressure of 100 atmospheres. In Germany these cylinders must be tested once a year. Not more than 1·11 kilo of the liquid is allowed in the cylinders per litre. The pressure exerted in the cylinders by the liquid chlorine is about 6–7 atmos., and the cylinders are tested up to 22 atmos. In Germany wagon-tanks are also used for the distribution of liquid chlorine.

When perfectly dry, chlorine does not attack cast- or wrought-iron, steel, phosphor, bronze, brass, copper, zinc, or lead.

---

[1] A disadvantage of electrolytic chlorine consists in its excessive chemical activity, which causes loss in the manufacture of chloride of lime, part of the chlorine being converted into $CaCl_2$, which is valueless, according to the following equation:

$$Ca(OH)_2 + Cl_2 = CaCl_2 + H_2O + O.$$

In order to avoid this loss, Sinding-Larsen (1898) has suggested heating the chlorine to 700° to 800° before the reaction with lime.

The specific gravity of liquid chlorine is 1·6725 at − 78·6°, 1·547 at − 30°, 1·468 at 0°, 1·314 at 50°, and 1·113 at 100°. T. Estreicher and M. Staniewski (1910) found the specific heat of liquid chlorine between − 80° and + 15·41° to be 0·2230 and that of solid chlorine between − 192° and − 108° to be 0·1446. The heat of fusion is 22·96 Cals. Its molecule consists of Cl_2. Organic substances are not ionised when dissolved in liquid chlorine, even when they form labile combinations with it, but a trace of hydrochloric acid suffices to render the liquid a conductor of the current.

ANALYSIS OF CHLORINE. It is necessary to determine the amounts of Cl, CO_2, and air. Two 100 c.c. burettes are each filled with the gas; in one the chlorine is absorbed by a solution of potassium iodide, and on titrating the liberated iodine with $\frac{N}{10}$ sodium thiosulphate solution (1 c.c. = 0·003546 grm. Cl = 1·1228 c.c. of Cl) its amount is found; the diminution of volume alone also shows the approximate volume of the chlorine. In the other burette chlorine and CO_2 are absorbed together with caustic soda solution; the difference between this and the former diminution of volume (with KI) gives the volume of CO_2; the remaining gas is air, which can be analysed if required in the Orsat apparatus (*q.v.*). The temperature and pressure of the gas have much influence on the result, and must, therefore, be taken into account (*see* pp. 23, 25, 35).

BROMINE : Br, 79.92

Bromine is a liquid which does not occur in nature in the free state, but is combined as bromides in many mineral deposits and also in sea water, especially in the Dead Sea, which contains 0·44 per cent. of bromine as sodium bromide, NaBr, and magnesium bromide, $MgBr_2$. The Atlantic Ocean contains only 0·0064 per cent.

It was first discovered by Balard in 1826, in the mother-liquors from the production of sea salt. In consequence of its presence in sea water it is found, together with iodine, in the ashes of certain marine plants (*kelp, varec*), from which it is obtained. It is now obtained in large quantity from the Stassfurt salts, and in the United States from the mother-liquors from the purification of rock salt.

PROPERTIES. Bromine is a dark red-brown liquid, which gives off brownish-red vapours of disagreeable, penetrating odour similar to that of chlorous acid. It has a specific gravity of 3·18, boils at 63°, solidifies at − 7·3°, and at − 20° is transformed into a lead-grey crystalline mass with metallic lustre. Bromine vapour has a normal density corresponding with the molecule Br_2, but at very high temperatures dissociation of the molecule into free atoms commences. With water at 0° bromine forms a red crystalline hydrate, $Br_2 + 10H_2O$, which decomposes at 15°; 100 parts of water dissolve 3·1 parts of bromine at 30°, 3·23 per cent. at 15°, and 3·6 per cent. at 5°.

Bromine water decomposes in the light, forming hydrobromic acid. Bromine is more soluble in alcohol, ether, and carbon disulphide than in water; it is still more soluble in solutions of HBr, KBr, and HCl (in HCl up to 13 per cent.).

Sulphuric acid of sp. gr. 1·795 dissolves Br in traces only. Bromine decomposes many organic substances with removal of hydrogen. It does not combine with free hydrogen under the influence of light alone, heat being also necessary. It does not combine directly with oxygen or carbon. The vapours of bromine react energetically with P, As, Sb, and Sn, even with production of flame. It has less affinity for the metals than chlorine. The bromine ions of bromides give, with silver nitrate solution, a slightly yellowish precipitate, less soluble in ammonia than silver chloride. Bromine has a strong corrosive action on the animal organism, and causes great irritation of the eyes. The bromides, on the contrary, are well tolerated by our organism, having a soothing action on the nerves and brain, and predisposing to sleep.

I. Guareschi (1912) discovered a very sensitive reaction for traces of bromine, even when in presence of chlorine and iodine. An aqueous fuchsine solution, decolorised by sulphur dioxide (Schiff's aldehyde reagent), is immediately coloured bluish-violet by traces of bromine. When the solution is shaken with ether, the colour separates between the two layers of superposed liquid—this does not happen with the aldehydes (which give a reddish-violet coloration). Guareschi's reaction is not influenced by nitrous vapours or CrO_2Cl_2.

USES OF BROMINE. Bromine is employed as an oxidiser in many chemical reactions instead of chlorine, *e. g.*, for transforming manganous oxide into the peroxide, potassium manganate into the permanganate:

$$2K_2MnO_4 + Br_2 = 2KMnO_4 + 2KBr,$$

and yellow potassium ferrocyanide into the ferricyanide:

$$K_4Fe(CN)_6 + Br = K_3Fe(CN)_6 + KBr.$$

Bromine is used for dissolving gold and separating it from platinum and silver. It is used as a disinfectant (4 grms. per cubic metre of space), and for this purpose Frank absorbs it in infusorial earth, forming small solid cylinders which are sold as *solid bromine.* Bromine is also employed for the preparation of bromine salts, for pharmaceutical and photographic purposes, and in the manufacture of aniline colours (eosine). It is also used as a depolariser in galvanic batteries.

STATISTICS AND PRICES. At first, in 1865, Stassfurt produced only 300 kilos per year, but the production soon increased enormously. In 1900 it rose to 500,000 kilos, was more than 717,400 kilos in 1905, and in 1906 amounted to 907,000 kilos, of which 171,000 kilos were exported, together with 644,000 kilos of bromides; in 1908 the United States imported 187,000 kilos of bromides. In 1905 Germany exported 634,000 kilos of bromine salts. The production in the United States was 182,000 kilos in 1880, and rose to 225,000 kilos in 1895 and 600,000 kilos in 1907, but the production had to be decreased to 500,000 kilos in 1908; in 1909 the production was 550,000 kilos, in 1910 425,000 and in 1912 320,000 kilos.

The price, which was at first £4 16*s.* per kilo, rapidly dropped to £2 8*s.*, then 12*s.*, and later 4*s.* per kilo. Then the desperate competition between Germany and the United States, which started in 1904, caused the price to drop rapidly to 1*s.* 7*d.* in 1907 and to 1*s.* in 1908. A partial understanding was arrived at in 1909 and the price of bromides was approximately doubled; in 1910 the price of bromine was 1*s.* 5*d.*, in 1911 1*s.* 10*d.*, and in 1912 2*s.* 6*d.* per kilo.

Italy imported 11,800 kilos in 1907, and 13,400 kilos (of the value of £1072) in 1908, 12,300 kilos in 1910, and 11,100 in 1911.

LABORATORY PREPARATION. Bromine is prepared by heating in a flask on the water-bath a mixture of sodium bromide, sulphuric acid, and manganese dioxide (or some other oxidising agent, such as potassium dichromate):

$$2NaBr + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + Br_2.$$

The oxygen of the oxidising agent combines with the hydrogen, which would otherwise form hydrobromic acid instead of bromine.

The red-brown vapours of bromine which are formed are condensed by passing into a long condenser.

In general the bromine may always be displaced from a solution of a bromide by means of chlorine (*see* Chlorine): $NaBr + Cl = NaCl + Br$.

To obtain highly pure bromine, the sodium bromide to be used must be purified by heating with bromine water to eliminate the iodine of the iodides;

the bromide obtained from the solution is then fused with a little potassium dichromate to get rid of chlorine and organic compounds. After this treatment, the salt yields pure bromine.

INDUSTRIAL PREPARATION. This industry has increased remarkably in recent years. From 1865 on the extraction of bromine has been carried out in the Stassfurt salt-works, and especially from the Magdeburg deposits, and later on from those of North America.[1]

The final mother-liquors from the treatment of carnallite ($MgCl_2$, KCl, $6H_2O$) (*see* Stassfurt Salts) contain on an average in each cubic metre 3·5 kilos of bromine, as $MgBr_2$, and about 300 kilos of $MgCl_2$.

At Neu Stassfurt the bromine is obtained by Pfeiffer's process; the hot mother-liquor falls as a fine spray from the top of a tower filled with fragments of stone or small silica balls, from the base of which a current of steam and chlorine ascends (Fig. 51). The chlorine is supplied by cylinders of the liquefied gas, and the rate of supply can be readily regulated.

The liquid rich in bromine which collects at the bottom of the tower descends into a stone boiler and is heated directly by superheated steam, which drives off the bromine together with a little dissolved chlorine. These vapours ascend the tower and pass from the upper delivery pipe into the spiral condenser, where they are condensed; the bromine collects together with water (bromine water) in a large glass bottle. The bromine vapours and chlorine which escape condensation are absorbed in a small tower at the side filled with moist iron filings or turnings, where they form iron bromide and chloride. At the side of the drawing, towards the top, the tubes which are fixed in a disc at the top of the main tower to convert the mother-liquor into the form of fine spray are shown on a larger scale. These tubes are cut away at the point and have a slit at the top to allow the liquid to enter.

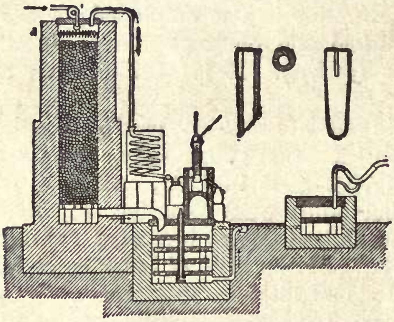


FIG. 51.

H. Dow (1891) employs instead of steam a current of air, which is passed through the solution saturated with bromine and carries this away as vapour. This method does not, however, appear to have been adopted industrially.[2]

---

[1] As early as 1846 the preparation of bromine was started in Pennsylvania and at Freeport, but to-day this manufacture has extended more especially in Michigan, Western Virginia, Ohio, and Pennsylvania, where the mother-liquors from rock salt are treated with dilute sulphuric acid and then concentrated, the hydrochloric acid evolved being condensed; on adding manganese dioxide and sulphuric acid to the concentrated liquid, bromine distils over, together with water and a little bromine chloride and bromoform; the whole is first condensed in an empty receiver, the vapours which escape condensation being absorbed in a second receiver with caustic soda solution. According to a patent of the Dow Chemical Co., the saline mother-liquors are partially electrolysed and the chlorine liberated in this way sets free the bromine, which is recovered by means of a current of hot air.

In Ohio the saline mother-liquors, of 35° to 40° Bé., contain a preponderance of $MgCl_2$, together with 0·5 to 1 per cent. of $MgBr_2$; instead of being treated with manganese dioxide, in this case potassium chlorate is used with the sulphuric acid in the exact quantity required theoretically to decompose all the bromide:

$$3MgBr_2 + 3H_2SO_4 + KClO_3 = 6Br + KCl + 3MgSO_4 + 3H_2O.$$

[2] Betts, in America, proposed in 1901 to remove the bromine from the mother-liquors, more especially when these are dilute, by means of pure carbolic acid; this at once precipitates crystalline tribromophenol: $C_6H_5OH + 6Br = 3HBr + C_6H_2Br_3OH$. Free bromine can be obtained from this compound by the action of chlorine or of sulphuric acid and iron, the phenol being regenerated in the latter case:

$$2C_6H_2Br_3OH + 3H_2SO_4 + 6Fe = 3FeBr_2 + 3FeSO_4 + 2C_6H_5OH.$$

One kilo of phenol (carbolic acid) precipitates 2·5 kilos of bromine. Practically this would result in a mixed process; a portion of the bromine would first be separated by the phenol, and the rest would be liberated by chlorine. One might also employ acetylene instead of phenol. These processes have not yet found practical application.

To free bromine from the small amount of chlorine which it contains it is agitated with iron bromide (obtained from the small tower) or with sodium bromide, or it is distilled. In the latter case all the chlorine passes over first, together with a little bromine, and this portion is collected separately from the rest of the distillate, which contains bromine only. Another method of purification consists in adding iron filings to the retort before distillation in quantity just sufficient to combine with all the chlorine present.

In 1890 G. Nahnsen took out a patent for the electrolytic production of bromine, and the process appears to have been worked industrially by Wünsche since 1895. It is based on the fact that when mother-liquors are electrolysed, even though they may contain chlorides in large quantity (*e. g.*, those from carnallite), these are not decomposed until all the bromine has been liberated. If the current is stopped at this point and the whole distilled, all the bromine will be obtained in the distillate. It is possible to work without diaphragms, but better yields are obtained with diaphragms and with the solution at a temperature of 80°. The current can be utilised with an efficiency of 70 per cent.; from forty-four baths in twenty-four hours 300 kilos of crude bromine are obtained. These baths are worked with a current of 150 amps. at 3·4 volts. This process is acquiring a certain amount of practical importance.

IODINE : I, 126.92

This element was discovered by Courtois in 1812 in the soda obtained from the ash of certain marine plants. It was named iodine in 1813 by Gay-Lussac, who studied its principal properties. Later on it was also studied by Davy.

Iodine is not found in nature in the free state, but always in combination; it accompanies chlorine compounds, and sometimes those of bromine. It is found together with other minerals in the form of HgI_2, AgI, PbI_2, and sodium iodate in Mexico and Chili; it is often found in association with the phosphorites and also with coal; it is found further in sea water and in mineral springs (*e. g.*, at Salsomaggiore, at Hall in Austria, etc.). In springs it occurs as MgI_2 and NaI, and rarely as KI or CaI_2. As salts of iodine are amongst the most soluble, they are dissolved by rain water, and this explains its frequent presence in mineral springs. Iodine is also found in certain vegetable organisms (*Fucus*, *Laminaria*, *Ulva*, etc.) and in some animals. It is found in notable quantity in Chili saltpetre.

CHEMICAL AND PHYSICAL PROPERTIES. Iodine is a crystalline solid, forming large rhombic plates, violet-black in colour, with metallic reflex. It has a similar odour to chlorine and bromine, colours the skin yellow, and acts as a corrosive, but less so than bromine. Its specific gravity is 4·95; it melts at 114°, forming a dark brown liquid which boils at 184°, producing violet vapours, which recondense without passing through the liquid state, but sublime in shining, black crystals. Its vapour density at 600° corresponds with the molecule I_2, but above 1500° complete dissociation into simple atoms take place.

Iodine is very slightly soluble in water (1 : 3600), but dissolves readily in alcohol (*tincture of iodine*) and also in an aqueous solution of KI. It is soluble in ether with a brown, and in chloroform and carbon disulphide with a violet coloration (carbon disulphide dissolves 18 per cent.).[1]

The chemical behaviour of iodine is analogous to that of chlorine and bromine, but its affinity for other elements is much weaker, and indeed iodine can be displaced from its compounds by both chlorine and bromine. It only combines with metals and with hydrogen on heating. It abstracts

---

[1] Hildebrand and Glascock (1909) have shown by cryoscopic experiments that the violet solutions of iodine are true solutions of iodine, whilst the brown ones are solutions of a labile combination of iodine with the solvent.

hydrogen from organic compounds (hydrocarbons) with difficulty. It gives a characteristic blue coloration with starch paste. If, for example, to a very dilute solution of KI starch paste and a few drops of chlorine water are added, a blue coloration is obtained immediately in the cold, owing to the liberation of iodine. On heating, the starch paste is decolorised.

Traces of iodides are detected by pouring the solution into a cylinder with 500 c.c. of water and adding two or three drops of fuming nitric acid and fifteen to twenty drops of carbon disulphide; on shaking the whole and allowing the carbon disulphide to settle to the bottom this will be coloured violet, as it dissolves the liberated iodine. Ciusa and Terni (1913) detect minimal traces of iodine in a very dilute iodide solution by the formation of a yellow precipitate when a little of the liquid is treated with a reagent obtained by dissolving 5 c.c. of nitric acid in 50 c.c. of water and then adding 60 c.c. of concentrated ammonia solution.

In the secretion of the thyroid gland (cartilage of Adam's apple) Baumann discovered and separated (1895) a product containing 9·3 per cent. of iodine, called iodothyrin, which has proved to be most efficacious in cases of goitre. It appears, in fact, that in districts where goitre is prevalent—*e. g.*, in Freiburg, in Baden, and in the Bergamasco valley—the thyroid glands are rather deficient in iodine. Iodine is, therefore, found in nature in true stable, organic combination. In Italy during the years of conscription, from 1896 to 1903, those exempted from military service on account of goitrous deformity numbered 27,554, that is, about 3500 per year, of which two-fifths were in Lombardy, one-quarter in Piedmont, and one-ninth in Venetia. It appears also, according to Carletti and Perusini (1908), that endemic cretinism is caused by goitrous condition of the mother, a fact which allows one to hope that it may be cured by the use of thyroiodin during pregnancy.

With silver nitrate the ions of soluble iodides form silver iodide, a yellow substance, insoluble in ammonia, in which silver chloride is readily, and silver bromide somewhat, soluble.

The physiological effect of iodides is to accelerate the metabolism of the organism. In very large doses they produce catarrhal inflammation of the mucous membranes; on prolonged use they may produce nervous disturbances. Iodine salts remove inflammation and swelling of the glands, but with corresponding enfeeblement of the system. Iodine was first used (Coindet, 1820) in medicine for curing goitre, and was later applied in the treatment of scrofula.

USES OF IODINE. Iodine is used in large quantities for photographic preparations (AgI and KI) and in the manufacture of various dyestuffs (tetraiodofluorescein, iodine green, iodine violet, cyanine, etc.). It is used medicinally as tincture of iodine and as potassium iodide; in the chemical laboratory it is used for various preparations, such as iodoform, iodole, methyl and ethyl iodides, hydriodic acid, etc.

STATISTICS AND PRICES. As early as 1838, 4 tons of iodine were obtained from algæ in France. In 1873, the French iodine industry treated 20,000 tons of ashes and employed 10,000 workpeople, the products being 50 tons of iodine, 4 tons of bromine, 2000 tons of potassium chloride, 720 tons of potassium sulphate, and 1800 tons of sodium chloride.

In the same year Britain (Scotland) produced 65 tons of iodine.

The European production of iodine is now 180 tons per year. In 1876 only 60 tons in England and 40 tons in France were obtained from kelp. Germany imported 377 tons in 1905; 297 tons in 1906; 194·2 tons in 1908; 369·3 tons in 1909; 362 tons in 1910; and 302 tons (235 from Chili, 22 from Peru, 14 from Norway, and 7·6 from Japan) in 1911. On the other hand, it exported 26·9 tons in 1905; 46 tons in 1906; 50·7 tons in 1908; and 59·2 tons in 1909. In 1911, Scandinavia exported 1806 tons of varec, of the value £10,000.

In South America the Chilian nitrate works produced :

In 1879 : 77 tons of iodine of the value of £220,000.
,, 1891 : 425 ,, ,, ,, £840,000 (about £20 per ton).
,, 1900 : 590 ,, ,, ,, £800,000 (about £13 12*s*. per ton).
,, 1904 : 460 tons.
,, 1911 : 506 ,,
,, 1912 : 512 ,, (65 tons direct to England, 264 to the European continent, and 183 to the United States).

Japan exported 1·8 tons in 1902, 15 tons in 1903, 30 tons in 1904, and about 50 tons in 1905; the greater portion is sent to the English market.

In 1914 the United States consumed 250 tons of iodine, the importation being 290 tons in 1910 and 210 tons in 1911.

To prevent a fall in prices an international syndicate has been formed which regulates the production by allowing it to be sold only for such purposes as admit of the payment of a high price; in this way the price has been forced up to £1 13*s*. 7*d*. per kilo. Japanese iodine is, however, now appearing on the market at competitive prices. Italy imported 32·4 tons of bromine and iodine together in 1904, 38·1 tons of iodine in 1906, 21 tons in 1907, 17·8 tons, of the value of £15,664, in 1908, 18·7 tons in 1909, 21·5 tons in 1910, and 17·5 tons (£17,500) in 1911.

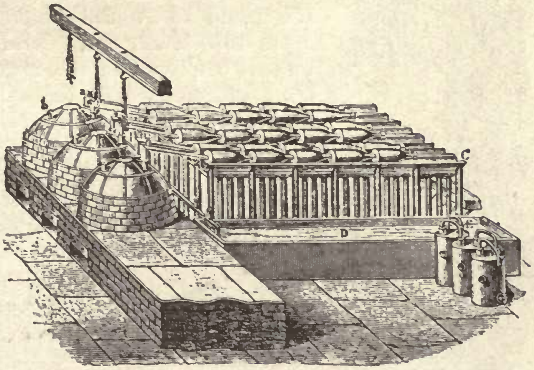


FIG. 52.

INDUSTRIAL PREPARATION. Iodine is scarcely ever prepared in the laboratory nowadays, as the industrially prepared product, previously purified by repeated sublimation (*vide infra*), is employed. Certain marine organisms accumulate iodine compounds, especially certain algæ which are thrown up by the waves on to the shore. In Japan these are worked up, especially the Laminaria species, containing 0·144 per cent. of iodine; *Ecklonia cava*, containing 0·140 per cent.; *Ecklonia bicyclis* and *Sargassum homeri* and *patens*, all of which contain less than 0·005 per cent.[1]

In Scotland the ashes of such algæ are called *kelp*, in Normandy *varec*, and they contain K_2CO_3, Na_2CO_3, K_2SO_4, KCl, NaCl, sulphites, thiosulphates, and NaI. One thousand kilos of *varec* give as much as 10·2 kilos of iodine, but during incineration (even when incomplete) of the algæ iodine is often lost. The ashes are extracted with water and the solution concentrated; NaCl and KCl separate first, and the sulphides and sulphites are then decomposed with sulphuric acid, with separation of sulphur. In one of Patterson's works the recovered sulphur amounts to as much as 100 tons per annum. The mother-liquors, containing much iodine, are distilled together with MnO_2 and H_2SO_4 by one of the following methods :

Two different forms of plant are in use on the large scale. The first consists of a series of cast-iron pans of 1·5 metres diameter (Fig. 52), with lead covers, in which the

---

[1] In Great Britain and Ireland use is made of the algæ and lichens which are torn from the rocks on which they grow and thrown up on the shores of the Atlantic after storms. Those growing at the bottom of the sea are : *Fucus digitatus*, *Laminaria digitata*, *Fucus saccharinus*, and *F. vesiculosus*, and those near the surface, *F. serratus*, *F. nodosus*, *F. filum*, etc.; the latter contain far less iodine than the former. The richest in iodine is *Fucus stenobolus* (cow's tail), with 0·022 per cent. of iodine in the ash; *F. stenophyllus* and *Laminaria digitata* contain 0·01 per cent., *F. bubosus* 0·001 per cent., *F. nodosus* 0·002 per cent., and *F. vesiculosus* still less. The composition of the ash derived by mixtures of these lichens is : 2·4–43·6 per cent. of K_2SO_4, 0·4–35 per cent. of KCl, 0·4–0·036 per cent. of KI, 20–35·5 per cent. of Na_2SO_4, 9–69·9 per cent. of NaI, and 0–16·7 per cent. of Na_2CO_3.

mother-liquors and sulphuric acid are heated. The distillate is collected and condensed in a series of five earthenware receivers (75 × 30 cms.) which are bottle-shaped and fit one into another. The manganese dioxide is added a little at a time, and the operation is finished when no further violet-red vapours are evolved on addition of a little more of this substance. About 70 kilos of iodine collect in each receiver in the form of crusts which can be detached and removed through the wider aperture.

In many processes and in many chemical industries iodides of Na, K, and Mg are obtained as by-products. In order to utilise these compounds they are treated in aqueous solution with a quantity of chlorine exactly corresponding with the amount of iodine present (Barruel's method): $KI + Cl = KCl + I$, and the free iodine which is formed is collected in the solid form at the surface or at the bottom of the vessel. If too little chlorine is used a small quantity of iodide remains which holds a portion of the iodine in solution, this escaping recovery. With excess of chlorine, iodine chloride is formed, together with iodates, which are soluble.

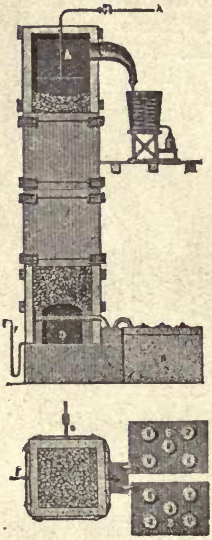


Fig. 53.

Both in the distillation process, which does not yield all the iodine, and in the chlorine process—in which the formation of ICl should be avoided—improvements have been introduced.

In 1880 Müller and Böckel proposed an apparatus analogous to that employed in the manufacture of bromine. In a tower filled with coke and stones (Fig. 53) the iodide solution falls from above and meets a current of chlorine and superheated steam from below. The iodine distils and is condensed in spiral condensers at the side.

In 1860 R. Wagner suggested acidification of the solution of the iodides with sulphuric acid and subsequent distillation in presence of ferric chloride:

$$NaI + FeCl_3 = NaCl + FeCl_2 + I.$$

In this case the formation of ClI, which is a source of loss, would be avoided.

Another very interesting method, which would eliminate all loss, would be the following: The iodide solution is evaporated to dryness and then treated with twice its weight of water; sulphuric acid and powdered potassium dichromate are then added and the whole well stirred. All the iodine separates in crystals, which are separated from the liquid and sublimed. The general reaction is as follows:

$$6NaI + \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 10H_2SO_4 =$$

$$\underset{\substack{\text{Potassium chromium}\\ \text{sulphate}}}{K_2Cr_2(SO_4)_4} + \underset{\substack{\text{Acid sodium}\\ \text{sulphate}}}{6NaHSO_4} + 7H_2O + 3I_2.$$

In 1886 Vitali advised the employment of an analogous reaction for treating the ashes of algæ (varec) directly; he advised that the algæ should be soaked in potash solution before incineration, in order to lessen the loss of iodine during that process. The ashes were then mixed with dichromate and heated to redness, the iodine distilling over:

$$6KI + K_2Cr_2O_7 = Cr_2O_3 + 4K_2O + 3I_2.$$

It appears that the yield of iodine from kelp is being much improved in some way, with simpler manipulation.

I. Boirault (Fr. Pat. 393,668 of 1907) treats aqueous solutions obtained from kelp with a solution of copper and ferrous sulphates: $2KI + 2CuSO_4 + 2FeSO_4 = K_2SO_4 + Fe_2(SO_4)_3 + Cu_2I_2$. The precipitated cuprous iodide is filtered off, dried, and decomposed by distillation with sulphuric acid and ferric oxide: $Fe_2O_3 + CuI + 3H_2SO_4 = CuSO_4 + 2FeSO_4 + 3H_2O + I$.

A still more rational method consists in the distillation of the dry algæ direct from a retort, avoiding incineration. This method was proposed by Standfort in 1864, and it was applied in a large Glasgow works. From 100 tons of dry algæ 1·3 tons of iodine, more than 28,300 cu. metres of illuminating gas (1,000,000 cu. ft.), and 1025 litres of paraffin oil were obtained.

As a further improvement the direct treatment of the moist algæ has been proposed, as if it rains during the drying on the shore part of the iodides is dissolved and lost.

In the United States a large company dries the marine plants at a temperature below 100° and then distils them in special furnaces below 400°; in this way the combustible volatile products, tar, etc., are recovered, while the ash is used for the extraction of the potassium salts.

In South America (Chili and Peru) iodine is obtained from crude sodium nitrate, which sometimes contains 0·2 per cent. in the form of sodium iodate, $NaIO_3$, and a little as NaI and MgI_2. The mother-liquors obtained during the refining of the nitrate contain as much as 0·5 per cent. of iodine. The solutions of nitre are treated with bisulphite or with sulphurous acid solution (Fauré, 1855):

$$2NaIO_3 + 5H_2SO_3 = 3H_2SO_4 + 2NaHSO_4 + H_2O + I_2.$$

The iodine separates as a solid black mass; a little chlorine water is then added to decompose any iodides and the impure iodine is collected on filters; it contains 80 to 85 per cent. of iodine. The filtrates are then used again to extract the remaining nitrate.

Instead of sulphurous acid the use of nitrogen trioxide, N_2O_3, obtained by burning a mixture of five parts of the nitrate with one part of carbon, has been proposed, but very serious difficulties were encountered in practice.

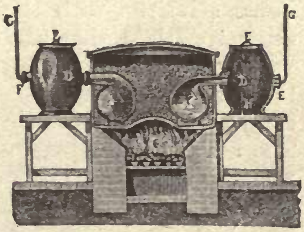


FIG. 54.

The nitrate mother-liquors are also treated on a large scale by separating the iodine in the form of cuprous iodide, Cu_2I_2. The liquors are mixed with sodium bisulphite (or ferrous sulphate or calcium sulphide) and copper sulphate; the iodine separates in the form of insoluble cuprous iodide which is marketed directly as such and valued according to its contents of iodine and of copper. A single works in Tarapaca produced 15 tons of copper iodide in 1873 and 50 tons in 1874. This method is suited to the separation of iodine from very dilute solutions of iodides. The iodine may also be separated as lead iodide.[1]

The *sublimation of crude iodine* is used for its purification, and is carried out in a terra-cotta retort immersed in a sand-bath (Fig. 54). It is heated gently in order to obtain large crystals and to ensure complete condensation of the vapours. These are condensed in large earthenware receivers, *D*, provided with a perforated false bottom to allow of removal of the water which accompanies the distillate. Iodine sublimed in this way is pure and contains only traces of water, Cl and Br. By subliming it a second time it is obtained in a very pure condition (resublimed iodine).

ANALYSIS OF IODINE. Pure resublimed iodine should be completely soluble in alcohol and in potassium iodide solution, and should leave no residue on sublimation. It is best analysed by dissolving 10 grms. in water and potassium iodide, making up to one litre and titrating 50 c.c. with a titrated solution of sodium thiosulphate, using starch paste as an indicator towards the end of the reaction (*see* Analysis of Chlorine).

---

[1] Many methods have also been tried to recover the small amount of iodine contained in the phosphorites treated by superphosphate works; the phosphorite is heated in closed chambers, and the vapours removed by a current of air and passed through a tower containing coke and iron in presence of steam. In this way iron iodide should be formed, which is soluble in water. Up till now, however, the yield of iodine is very small and the greater part of it remains in the phosphorite.

HYDROGEN COMPOUNDS OF THE HALOGENS (HYDRACIDS)

The hydrogen compounds of the halogens are all acids and are called hydracids, to distinguish them from another category of acids which contain both hydrogen and oxygen, and are called oxy-acids.

Each atom of the four elements: F, Cl, Br, I, combines with a single atom of H, forming the following four very powerful acids:

HF	HCl	HBr	HI
Hydrofluoric acid	**Hydrochloric acid**	**Hydrobromic acid**	**Hydriodic acid**

Their reactivity diminishes with increase of the molecular weight. They are all gaseous, but are readily liquefied by refrigeration or pressure. In concentrated aqueous solution they fume in the air, because the small quantities of acid evaporating dissolve in the water vapour in the atmosphere to form a solution which is more dilute and has a lesser vapour pressure than the more concentrated acid from which it is formed; it is therefore obliged to condense in small globules which form a cloud. Dilute solutions of these acids do not fume in the air, because the acid which evaporates spontaneously forms solutions with the moisture of the atmosphere which are more concentrated than the solutions from which they are derived, have a higher vapour pressure, and therefore do not condense in globules. In dry air even the concentrated solutions do not fume. The vapour density of these acids compared with hydrogen corresponds with their normal molecular weights. The affinity of hydrogen for the halogens diminishes with increasing atomic weight of the latter. HF is very stable, HCl decomposes at 1500°, HBr already at 800°, and HI at a little above 400°. The metallic derivatives (salts) of the halogens behave in an analogous manner, in respect to their solubility and stability; thus, silver chloride is white and soluble in ammonia, silver bromide pale yellow and sparingly soluble in ammonia, and silver iodide deep yellow and insoluble in ammonia.

These gaseous acids are extremely soluble in water, but they do not apparently follow Henry's law, the greater portion of the acid dissolving almost independently of the pressure. One portion of the acid dissolved in the water is dissociated into its component ions, and this portion does not follow Henry's law as it is no longer a gas and has no longer the same composition as the original acid; the other portion is dissolved without dissociation, and this portion does obey the above-mentioned law. In the typical case of hydrochloric acid we observe that whilst the pure anhydrous acid boils at — 83°, and water at 100°, when the acid and water are mixed in various proportions the resultant liquid does not always boil at an intermediate temperature (between — 83° and 100°); the boiling-point of dilute solutions containing less than 30 per cent. of HCl is higher than 100°, while a 20 per cent. solution has the maximum boiling-point of 110°. If, then, a concentrated solution of hydrochloric acid is distilled, all the acid which boils at lower temperatures than 110° is gradually boiled off and the temperature steadily rises until the acid which remains contains only 20 per cent. of HCl (with the maximum boiling-point) and the acid which now distils is of constant composition. Also if, on the contrary, an acid containing less than 20 per cent. of HCl is distilled, at first the distillate consists of acid boiling at a lower temperature and the boiling-point rises in this case also until it reaches 110°, when an acid containing 20 per cent. of HCl remains and distils unaltered. It might be supposed that this acid, boiling at a constant temperature, was a true chemical compound of water and acid, to which the formula $HCl, 8H_2O$ could be assigned, but this is not the case, because the composition of the constant boiling-point acid varies with the pressure at which the distillation is conducted. In fact we may state generally that any solution of a gas which has a boiling-point higher than those of slightly more and slightly less concentrated solutions will distil without changing its composition.

HYDROFLUORIC ACID : HF

PROPERTIES. Hydrofluoric acid is a colourless gas of pungent odour, fuming in the air. On the skin it produces blisters and ulcerous wounds, difficult to cure; these should be at once washed with a very dilute aqueous solution of ammonia. It is strongly poisonous, and when inhaled in some quantity is sometimes fatal. The symptoms of poisoning with this acid are nausea, vomiting, and excessive salivation.

In the cold it condenses to a colourless liquid boiling at 19·5°; it solidifies at — 102° and melts at — 92·5°. On heating a concentrated aqueous solution of this acid it first evolves pure HF, and a liquid remains which distils unchanged at 120°, containing 38 per cent. of HF (corresponding with the formula $HF + 2H_2O$, *see above*). It chars cork, paper, and wood, attacks glass strongly and rapidly, but does not attack paraffin wax, beeswax, resin, platinum, or gold, and acts only slightly on lead. It is very soluble in water, and the solution, which also attacks glass strongly, is kept in vessels of platinum, gold, lead, or guttapercha (or vulcanite), or in glass vessels lined with paraffin wax.

Its action on glass is shown by the following experiment. Powdered calcium fluoride is treated with an excess of strong sulphuric acid in a platinum or lead capsule, which is covered with a sheet of glass covered with wax in which words or figures have been incised. The reaction takes place in half an hour even in the cold. The gaseous HF leaves an opaque mark where it has attacked the glass; in aqueous solution, on the other hand, the attacked portions are transparent.

Hydrofluoric acid is a bad conductor of electricity. At — 25° it does not attack metals or non-metals (except the alkali metals). It combines energetically with anhydrides (sulphuric and phosphoric anhydrides, etc.), and displaces all the other halogens from their salts. It reacts energetically with silicates (glass) and on silica, dissolving it in the form of silicon fluoride, SIF_4:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

From the electrical conductivity of sodium fluoride the dibasicity of the acid has been deduced (1907) and it should now be written H_2F_2 (*vide supra*). Its power of inverting sugar is marked.

Whilst the other halogen salts of silver are insoluble in water, silver fluoride is soluble. On the contrary, whilst the chloride, bromide, and iodide of calcium are easily soluble in water, calcium fluoride is insoluble. The heat of formation of gaseous HF is 161·7 Kj. (38,600 cals.), and its heat of solution 49·4 Kj. (11,907 cals.).

USES OF HYDROFLUORIC ACID. This acid is used in glass-works to mark graduated apparatus, such as thermometers, cylinders, flasks, etc. In analytical chemistry it is used for decomposing silicates and rendering them soluble. An opaque etching on glass is obtained by mixtures of certain soluble fluorides with other white, insoluble substances.

In 1899 Malinsky proposed the use of hydrofluoric acid for the hydrolysis of starch, in order to transform it into sugar (glucose) (*see* Vol. II., " Organic Chemistry ").

Hydrofluoric acid is employed in large quantity in the manufacture of spirit from cereals by Effront's process (*see* Vol. II.). It is very destructive to vegetation, and is a potent antiseptic.

PRICES OF HYDROFLUORIC ACID AND CONTAINING VESSELS FOR THE SAME. Commercial fuming hydrofluoric acid ordinarily contains 60 to 65 per cent. of HF (30° to 33° Bé.) and is sold at 8½*d.* to 9*d.* per kilo or in large quantities at

£2 4*s*. to £2 8*s*. per 100 kilos. The commercial quality, free from arsenic, containing 40 per cent. of HF (20° Bé.), costs 10*d*. per kilo and £2 12*s*. per 100 kilos. The purer quality for medical use (50 per cent. = 25° Bé.) costs about double. Chemically pure fuming HF, distilled in platinum, costs up to 5*s*. per kilo; the common fuming acid for writing on glass costs 1*s*. 3*d*. per kilo.

Guttapercha bottles for holding HF of 100 c.c. capacity cost 1*s*. 3*d*., of 1000 c.c. capacity 5*s*. 10*d*., of 10 kilos capacity £2 8*s*., and of 40 kilos capacity up to £6.

Ordinarily the greater portion of the HF sold is kept and sent out in vessels of lead or of lead-lined iron. Lead vessels of 5 kilos capacity cost 12*s*., of 40 kilos capacity £1 6*s*. The proposal has recently been made (1907) to store and send out hydrofluoric solutions in beer barrels lined internally with pure resin.

A single factory in Vienna produces 5 tons of hydrofluoric acid per day (1908). The official statistics for Italy show a production of 70 tons in 1906, 50 in 1907, 35 in 1908, and only 7 in 1911, the importation having increased in consequence of the cessation of the manufacture by the firm of Carlo Elba in Milan.

PREPARATION. Hydrofluoric acid was first prepared in the pure state as a liquid by Scopoli in 1784; he preserved it in silver vessels gilt inside, but did not know its chemical composition. As early as 1670 Schwankhald used fluorspar with sulphuric acid for etching glass.

Hydrogen combines with fluorine even in the dark, and this reaction takes place much more readily than that between hydrogen and chlorine.

In 1856 Fremy prepared anhydrous hydrofluoric acid by drying potassium hydrogen fluoride, KF, HF, first at 100° and then finally for fifteen days in an evacuated desiccator containing strong sulphuric acid and fused caustic soda. The dry substance was then distilled from a platinum retort at a gentle heat and the product collected in platinum receivers cooled with snow and salt.

Louyet prepared anhydrous HF by heating silver fluoride (AgF) in a current of hydrogen: $AgF + H = Ag + HF$.

HF is also obtained on passing a current of hydrogen sulphide gas over lead fluoride: $PbF_2 + H_2S = 2HF + PbS$.

In the laboratory it is commonly prepared by distilling powdered calcium fluoride with excess of strong sulphuric acid (*see below*) from a small retort of lead or platinum, the receiver in which it is collected being well cooled.

INDUSTRIAL MANUFACTURE. Fluorspar is decomposed by strong sulphuric acid according to the following equation:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

or cryolite by sulphuric acid:

$$2AlF_3, 3NaF + 6H_2SO_4 = 2Na_2SO_4 + 2AlNa(SO_4)_2 + 12HF.$$

HF is ordinarily prepared industrially in horizontal cast-iron cylinders holding a charge of as much as one ton of powdered calcium fluoride and one ton of strong sulphuric acid of 66° Bé. The acid, which is evolved on gentle heating, is condensed in large spiral condensers of lead and collected in lead receivers, and has a concentration of 40° Bé. (70 per cent. HF). At first silicon fluoride, SiF_4, also distils and deposits gelatinous silica on reacting with water in the first receiver; this is therefore changed shortly after the commencement of the distillation.

Hampel adopts the following apparatus (Fig. 55): A cast-iron retort holding the charge ($CaF_2 + H_2SO_4$) communicates by means of an iron tube with a tower filled with wood-charcoal; this is surmounted by a large pan (or tank) with a perforated bottom, which is filled with water, causing a fine spray to fall on to the carbon below. The lower portion of the tower is cooled by a lead coil through which cold water flows; this causes the hydrofluoric acid to condense and dissolve readily and the liquid is collected in a separate lead receiver. Städeler recommended bottles of guttapercha as being economical for the collection and preservation of hydrofluoric acid, but it has been found that in time they contaminate the acid. Ebonite bottles are better. Vessels of metal and glass, coated internally with paraffin wax, also serve fairly well.

It is not to be denied that even with well-closed vessels a little HF often escapes and attacks external objects.

If the hydrofluoric acid contains H_2S, formed from sulphides in the fluorspar, it becomes turbid after a short time through separation of sulphur.

To obtain it pure for laboratory use, starting from the commercial product, the lead is first removed with H_2S, and hydrofluosilicic acid then removed with K_2CO_3; it is then filtered and the H_2S removed with silver carbonate. By distilling in a platinum apparatus pure HF is then obtained.

Thorpe and Hambly distil the commercial acid with potassium permanganate, and then transform the HF into hydrogen potassium fluoride, KHF_2, by means of K_2CO_3 or KOH; they then dry the HF, KF and distil it, collecting the hydrofluoric acid in distilled water.

ANALYSIS OF HYDROFLUORIC ACID. A given quantity, removed with a pipette internally coated with wax—the capacity of which has been previously measured—is treated in a platinum capsule with excess of normal caustic soda solution free from carbonate; the excess of sodium hydroxide is then titrated back with normal sulphuric acid, phenolphthalein (*not* litmus or methyl orange) being used as indicator. 1 c.c. N NaOH = 0·020 grm. HF.

Silicon fluoride is often present as an impurity, and is detected by adding potassium acetate to a given quantity of the hydrofluoric acid and evaporating it to dryness on the water-bath. That part of the residue which is insoluble in water consists of potassium fluosilicate.

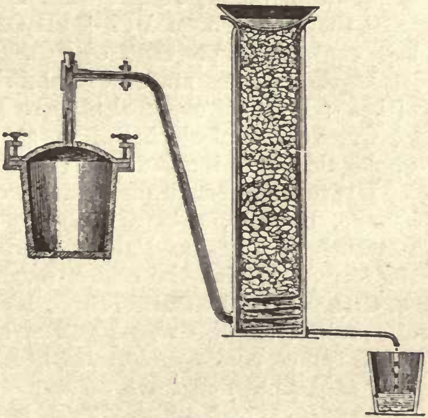


FIG. 55.

HYDROCHLORIC ACID : HCl

The Arabian alchemists employed this acid mixed with nitric acid, as *aqua regia*, but did not know it in the pure condition.

The *aqua regia* was obtained by distilling saltpetre, ammonium chloride, and ferrous sulphate.

In the fifteenth century Basil Valentine described hydrochloric acid for the first time, calling it spirits of salt. He obtained it in aqueous solution by distilling iron sulphate and NaCl.

In the seventeenth century Glauber obtained it by distilling NaCl with sulphuric acid. Stephen Hales obtained it by the action of H_2SO_4 on ammonium chloride.

Hydrochloric acid was prepared pure by Priestley, who considered it to be an oxidised acid of *murum*, as chlorine was then called, and therefore named it muriatic acid. It was not until 1810 that Davy showed that hydrochloric acid was a hydrogen derivative of chlorine.

This acid is found in nature in volcanic exhalations, for example, in those of Vesuvius. It is found in the water of the Vinagro River which issues from the volcano Purace, in the Andes, and contains 0·111 per cent. of HCl, from which it is estimated that thirty tons of this acid are removed by the river each day. It has also been found in an acid spring near the volcano Paramo de Ruiz, in New Granada, the water of which contains 0·88 per cent.

Hydrochloric acid is a normal constituent of the gastric juices of all mammals and serves an important function in digestion. The gastric juice of the dog contains 3 per cent.; that of man 0·05 to 0·32 per cent.

PHYSICAL PROPERTIES. Hydrochloric acid is a colourless gas of acrid, pungent odour, and fumes in the air. Its critical temperature is + 52·3°, and its critical pressure 86 atmospheres. When liquefied it has a specific gravity of 0·83 at 15°; it is solid at − 115°, and boils at − 83°. In 1846 Faraday liquefied it for the first time, under pressure, with a mixture of solid carbon dioxide and ether.

The density of the vapour or gas of hydrochloric acid, compared with air, is 1·26 at 0° and 760 mm. pressure, and a litre of the gas weighs 1·6288 grms. It colours blue litmus paper red. It readily dissolves in water in the proportion of 450 vols. in 1 vol. of water.

Aqueous hydrochloric acid saturated at 15° contains 43 per cent. of HCl, and has the specific gravity 1·212. When the concentrated aqueous solution is distilled, much HCl is first evolved, and then at 110° an acid of constant composition (about 20 per cent. HCl, *see* p. 166) distils, which corresponds with the composition $HCl + 8H_2O$. The ordinary commercial hydrochloric acid contains 35 per cent. of HCl.

In the gaseous state it is absorbed by wood charcoal with development of heat; 1 vol. of charcoal absorbs 165 vols.

One volume of alcohol of sp. gr. 0·836 dissolves 327 vols., and the volume of the alcohol is increased to 1·324 vol.

Hydrochloric acid dissolves also in methyl alcohol, acetic acid, ether, hexane, benzene, xylene, etc. An alcoholic solution of HCl has only one-sixteenth of the electrical conductivity of the aqueous solution, because in the former solution the acid is much less dissociated into its ions.

CHEMICAL PROPERTIES. Electrolysis shows that HCl is composed of 1 vol. of chlorine and 1 vol. of hydrogen.

It is not combustible, and is not a supporter of combustion, excepting that of sodium and some other metals, when they are once burning. When concentrated hydrochloric acid is saturated with gaseous HCl at − 22°, crystals of a hydrate, $HCl, 2H_2O$, separate, which melt at 18°, with evolution of HCl. When two parts of snow are mixed with one part of concentrated commercial HCl, the temperature is lowered by 15°. *Aqua regia* is formed by mixing 3 vols. of HCl with 1 vol. of concentrated HNO_3, and dissolves all the metals, including gold and platinum.

When dissolved in water hydrochloric acid is a strong monobasic acid which readily dissolves the alkali and alkaline earth metals and also Mg, Zn, Cd, and Fe at the ordinary temperature, with evolution of hydrogen. When heated it dissolves Pb, Cu, and Hg, also with evolution of hydrogen. In all these cases the corresponding chlorides are formed, which may also be obtained by the action of HCl on the metallic oxides and carbonates. The metallic chlorides are almost all soluble in water, with the exception of AgCl, Hg_2Cl_2, and Cu_2Cl_2, and also $PbCl_2$, which is only slightly soluble. At a red heat almost all the metallic chlorides volatilise unchanged, excepting those of Au, Pt, and Ir, which are decomposed.

Anhydrous liquid hydrogen chloride is a transparent, colourless, rather mobile liquid which has no action on metals, even on Zn, Mg, and Fe, although these are easily attacked by its aqueous solution. With powdered aluminium, however, hydrogen is evolved; further, it does not react with calcium oxide, with sulphides, or with metallic carbonates, and it does not even redden dry litmus paper.

HCl acts as a poison on plants, and air containing only 3·5 parts per thousand is fatal to many animals. Human beings cannot for long tolerate the respiration of air containing 0·5 part per thousand of HCl.

USES OF HYDROCHLORIC ACID. Hydrochloric acid is often used for the preparation of chlorine, ammonium chloride, and many other chlorides, for the purification of animal charcoal from carbonates, for the manufacture of glue, and for etching. It is also used for the preparation of carbon dioxide, the extraction of cupriferous minerals, and for other metallurgical purposes. Large quantities are used by manufacturers of dyestuffs (in the preparation of the hydrochlorides of aniline and other amines) and pigments, and also for the manufacture of many chlorinated organic chemicals.

Since excess of hydrochloric acid is often available, it is proposed to utilise it, for example, to replace sulphuric acid in the electrolytic refining of copper, and so save 50 per cent. of the electrical energy expended. Moltraut (French patent No. 408,440) advises its use in diluted condition—in place of lime and sodium sulphide—for unhairing hides; for etching brass it is also to be preferred to sulphuric acid.

STATISTICS AND PRICES. In 1895 the European production of hydrochloric acid was about two million tons, of which one-half was produced in England, which in 1908 contained sixty-five works. In 1882 Germany produced and consumed 148,450 tons, in 1901 almost 300,000 tons, in 1906 350,000 tons of the value of £800,000, and in 1910 about 450,000 tons of 30 per cent. acid, valued at nearly a million pounds sterling. In 1909 Germany imported 4923 tons of hydrochloric acid and exported 15,992 tons. In 1908 Russia produced 50,000 tons. In Italy the production of hydrochloric acid amounted to 4600 tons in 1893; 8680 tons in 1903; 11,170 tons in 1905; 12,021 tons in 1906; and 14,170 tons in 1908, of the value of £33,600. Italy imported 96 tons in 1906, 218 tons in 1908, and 40 tons in 1911, when 25 tons were exported. It is a notable fact that the price of hydrochloric acid has occasionally exceeded that of sulphuric acid. In small quantities the price of crude hydrochloric acid of 20° Bé. (32 per cent. HCl) is 3*s.* 9*d.* to 4*s.* per cwt., and in large quantities as little as £2 per ton; acid free from arsenic and sulphuric acid costs £4 16*s.*, chemically pure acid of sp. gr. 1·19 (23° Bé.) as much as £14, and the same of 19° Bé. about £10 per ton.[1]

---

[1] Th. Meyer gives the cost of manufacture of hydrochloric acid in Germany, prior to 1910, as follows:

Plant:	£	s.
Ground, 600 sq. metres	152	0
Factory and condensation sheds, 600 sq. metres	750	0
Muffle furnace and cast-iron pan	475	0
Apparatus for preliminary cooling	140	0
Absorption battery with end towers	335	0
Flooring, etc	148	0
Total	£2000	0

Working costs:	£	s.
1235 tons of 97·5% rock salt (= 1204 tons NaCl) at 12*s.* per ton	741	0
1275 ,, 78% sulphuric acid (60° Bé.) at £1 per ton	1275	0
62 ,, bisulphate, for decanting the salt, at 10*s.* per ton	31	0
445 ,, coal at 17*s.* 2*d.* per ton	383	0
Various apparatus, lighting	50	0
Repairs	179	0
Labour, 5 workpeople for 330 days at 4*s.* per day	330	0
Staff and overseers	150	0
Interest on plant, 4% on £2000	80	0
Sinking fund on factory, 5% on £750	37	10
,, ,, building materials, 10% on £1250	125	0
Total	£3381	10
Value of 1485 tons of sulphate obtained, at £1 8*s.* per ton	2079	0
Cost of 2100 tons of hydrochloric acid (20° Bé.)	£1302	10

Hence 1 ton of the acid costs 12*s.* 4*d.*, exclusive of general expenses.

The cost of hydrochloric acid depends especially on the prices of sulphuric acid and salt. To economise in sulphuric acid, use is largely made now of sodium bisulphate mixed with a little sulphuric acid. This bisulphate process was first studied and applied by Oehlar and Th. Meyer (German patent No. 186,398), who constructed a furnace with mechanical mixing for the bisulphate and the finely-ground salt; the process is a very economical one.

The consumption of hydrochloric acid in the United States in various industries in 1900 and in 1905, in which years the productions amounted to 65,000 and 90,000 tons respectively, was as follows:

	1900	1905
For bleaching textiles	450 tons	500 tons
,, chrome tanning	2,400	2,900
,, cleaning the façades of houses	1,500	2,000
,, disinfection	1,200	1,500
,, dyes	3,250	3,800
,, fine chemicals	550	555
,, ordinary chemicals	1,700	6,500
,, glucose manufacture	5,400	6,100
,, glue manufacture	19,000	3,700
,, pickling olives	1,250	1,700
,, paper manufacture	1,500	2,000
,, roasting metals	13,200	14,500
,, reducing and refining metals	7,500	12,200
,, soap-making	200	190
,, soldering	2,000	1,450
,, textile industries	2,900	3,400
,, washing boneblack	700	800
,, ,, sand and clay	700	950
,, various purposes	650	900

PREPARATION IN THE LABORATORY. Equal volumes of chlorine and hydrogen combine at 150°; they also combine at the ordinary temperature under the influence of the electric discharge, or in contact with spongy platinum, or under the influence of chemically active light rays, for instance, sunlight or the light obtained by burning a mixture of nitric oxide and carbon disulphide vapour, or by burning magnesium. The combination occurs with development of heat and light. Hydrogen burns in an atmosphere of chlorine yielding HCl. Various chlorides of the non-metals decompose with water at the ordinary temperature giving HCl, *e. g.*, the chlorides of S, N, P, Sb, Bi, and Si. Thus

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

HCl is also formed when certain organic compounds containing chlorine are burnt; thus on soaking a little cotton wool in a mixture of alcohol and chloroform and setting fire to it the vapours emitted contain hydrochloric acid (recognisable by its action on litmus paper), which is formed from the hydrogen and chlorine of the organic substances.

When metallic chlorides are heated with strong acids HCl is formed.

The ordinary method of preparation is based on the action of sulphuric acid on NaCl. At comparatively low temperatures the first phase of the reaction takes place:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

On then heating to redness there is the further reaction:

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

In the laboratory HCl is prepared as follows, only the first phase of the reaction being used:

The sulphuric acid and salt are placed in a flask heated on a sand-bath (Fig. 56), and the escaping HCl gas is passed over the surface of water in the three Woulff's bottles united by tubing above and also by side tubes below, a current of water flowing through the bottles in a contrary direction to the gas. A concentrated HCl solution is thus obtained and the escaping gas is condensed in a tower filled with porous material down which water is sprayed. The dilute solution so obtained is continuously concentrated by passing through the three Woulff's bottles, in the first of which, containing the largest quantity of gas, concentrated aqueous HCl is formed.

INDUSTRIAL MANUFACTURE OF HYDROCHLORIC ACID. Until the commencement of the nineteenth century this substance was prepared by distilling sulphuric acid with sodium chloride in cylindrical cast-iron retorts and absorbing the hydrochloric acid gas which was evolved in a battery of receivers with two necks, half full of water. In certain localities this method is still used for small scale production, but the greater part of the hydrochloric acid is now obtained as a secondary product in the manufacture of sodium sulphate, which is itself used in the manufacture of sodium carbonate by the Leblanc process.

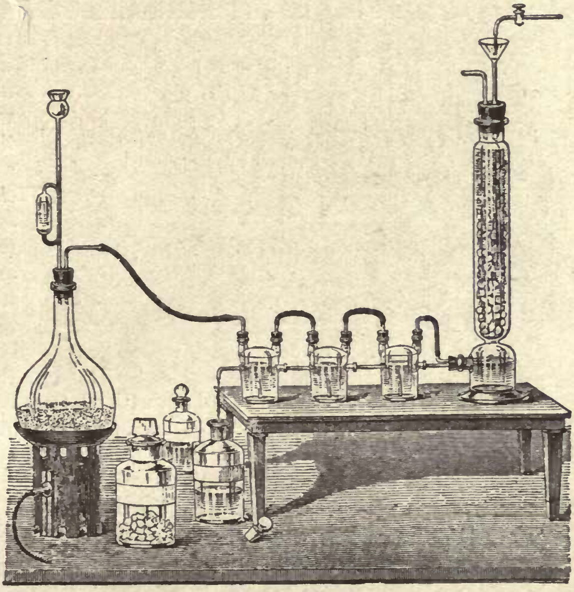


Fig. 56.

The reaction of the H_2SO_4 on NaCl takes place in two phases in the so-called salt-cake furnaces. The first phase takes place at a relatively low temperature in a compartment of the furnace of which the bottom is formed by a pan of lead or cast-iron which is heated moderately by the hot gases from the hearth (Fig. 57). Into this pan are introduced the salt and the corresponding quantity of sulphuric acid of 52° Bé. or, better, 62° Bé. (*e. g.*, that from the Glover towers of sulphuric acid plants). When heated, the mass liquefies and simultaneously develops the first part of the HCl, becoming denser, until sodium bisulphate remains: $NaCl + H_2SO_4 = NaHSO_4 + HCl$. The gas is passed through long earthenware pipes which communicate with a battery of double-necked earthenware receivers (*bonbonnes, tourilles*), illustrated in Figs. 60 and 61. When the central pan no longer develops HCl, as is shown by the lower temperature of the delivery pipes, the pasty mass is passed into two lateral compartments of the furnace, where it is heated to redness by the direct action of the flame and furnace gases. The bisulphate (sodium hydrogen sulphate) formed in the pan reacts at this temperature with the remaining portion of the NaCl, and the second phase of the reaction occurs with formation of hydrochloric acid and neutral sodium sulphate: $NaHSO_4 + NaCl = Na_4SO_4 + HCl$. In this portion of the furnace it is necessary to stir the mass by means of suitable iron tools, which are introduced through the openings shown in Fig. 57; the gas is thus completely evolved. The hydrochloric acid developed during this second phase is much less pure, being mixed with the furnace gases, and is, therefore, condensed in a separate battery of receivers (*see* Figs. 59 and 60). These furnaces with direct flame are called *reverberatory furnaces*.

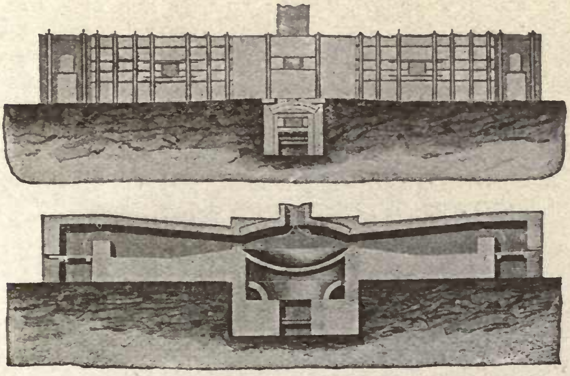


Fig. 57.

In modern furnaces the compartment where the second phase takes place is arranged as a *muffle furnace* (Fig. 58) with a reverberatory arch, *B*. These muffles do not communicate directly with the hearth, but are heated indirectly from outside, as the furnace gases turn and pass between the double walls of brickwork, *f*. By means of muffle furnaces the advantage is gained that the HCl is obtained in a stronger and purer condition, and is, therefore, absorbed more easily, whilst in the old furnaces with direct flame it was obtained mixed with all the products of combustion and with air, which rendered complete absorption difficult. The hot gases from the hearth, *a*, after heating the muffle, pass under it and through the flue, *g*, and then heat the pan, *A*, in which the first phase of the reaction takes place, before passing away to the chimney through *q*.[1]

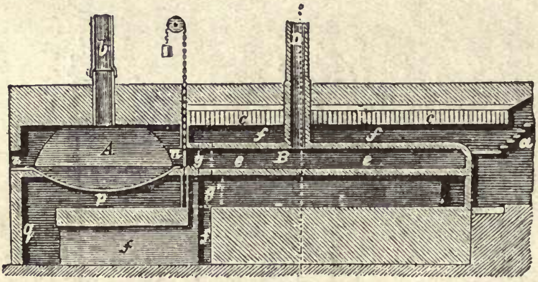


FIG. 58.

Nowadays muffle furnaces are fitted not with a lateral hearth, but with a producer lower than the furnace, so that the gases passing upwards attain a certain pressure round the muffle and any small cracks in the latter thus allow no HCl to escape. The producers are similar to those used in gas-works for heating the retorts and the gas generated ignites in the space above the muffle, hot air which has passed over the very hot top of this

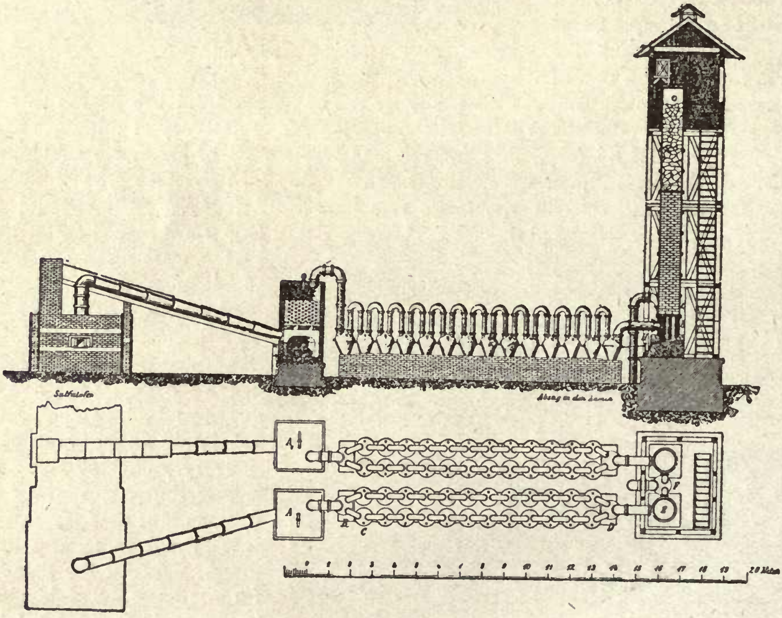


FIG. 59.

---

[1] A rational method of distributing the hot furnace gases uniformly under the pan was proposed in 1898 by Th. Meyer, based on the same principle as his tangential lead chambers (*see below*, Sulphuric Acid Manufacture). With large plants, two pans, with one furnace between them, are sometimes used. One pan is charged two hours after the other and the material is kept in the pans for four hours before being discharged into the muffle, which thus receives material every two hours. Since the pans are hot when charged, vigorous evolution of hydrogen chloride takes place, this being sometimes accompanied by frothing, which may pass into the condensing battery; this formation of froth may be avoided by addition of 1–2 kilos of oil with the salt.

space being drawn in. A ventilator regulates this hot air current in accordance with the chemical composition of the gas from the generator. This method effects an economy of 26–30 per cent. over heating with coal in the ordinary way. Frequent rupture of the earthenware piping carrying the hot HCl vapour from the furnace to the absorption battery is often avoided by the use of pipes of volvic stone, which withstands rapid changes of temperature.

The acid is absorbed in a battery of receivers communicating with one another as in Fig. 59, which illustrates a complete hydrochloric acid plant, and shows the long delivery pipe from the pan, the other delivery pipe from the muffle, the first condensing and purifying tower, *A*, where the sulphuric acid carried over by the gases is caught and the gases which issue from the furnace at a temperature of 200° to 250° are cooled; then follow the receivers, which are fed with a continuous stream of water from the final condensing towers, which absorb the last traces of HCl by means of a water-spray before the gases pass away into the atmosphere.[1] Even when muffle furnaces are used the acid is absorbed in two batteries of receivers as the HCl from the pan is purer than that from the muffles. The most concentrated acid, which collects in the first receivers, attains a density of 20° to 22° Bé. and is thus placed on the market. The acid which collects at the base of the towers has a density of 7° to 8° Bé., and is passed into the receivers, where it travels in the reverse

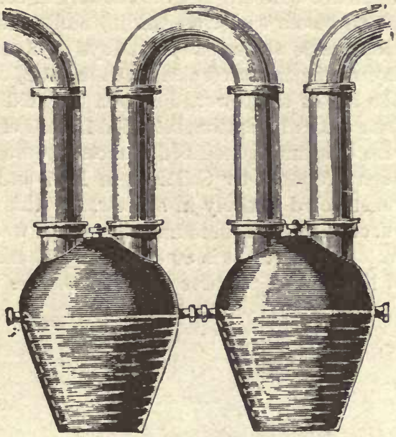


FIG. 60.

---

[1] *Legislation regarding hydrochloric acid works.* In the early days of the manufacture of sodium sulphate for use in the manufacture of carbonate the HCl was not utilised and was allowed to pass away into the atmosphere. The complaints which arose in the neighbourhood of these works induced the manufacturers, especially in England, to erect very high chimneys, in the hope that the HCl when carried to a great height would mix with large quantities of air and cause no more trouble (at St. Rollox a chimney 150 metres high was constructed). These hopes were, however, not realised, because the HCl, being heavier than air, redescended to earth, extending over the adjacent country as a thick mist and causing serious damage, especially to vegetation. The manufacturers were obliged to condense the HCl in order to remove the nuisance, and as at that time they had no use for the product, they passed the fumes through long channels in which they were washed with water. A large portion of the gas still escaped into the atmosphere, and the dissolved portion was also largely given off again as fumes. In 1836 Gossage first proposed the absorption of the HCl in a rational manner in condensing towers filled with coke moistened from above with a spray of water. By this means the condensation was much more thorough, but was still incomplete, owing to irregular supervision; on the other hand, the production of sodium sulphate increased to such an extent that the absolute quantity of hydrochloric acid in the atmosphere remained unaltered in spite of the fact that it was largely condensed. The continuance of these nuisances led to complaints which necessitated restrictive legislation. In 1855 a law was passed in Belgium which made compulsory the employment of muffle furnaces instead of those with direct flame, as in the latter the escape of HCl was greater. It was actually found that, whilst in 1854 only 75–85 kilos of hydrochloric acid were obtained from 100 kilos of salt, in 1870 the same works obtained on the average 120–160 kilos.

In England a law was passed in 1863 which forbade the escape from the condensing towers of more than 5 per cent. of the hydrochloric acid introduced, as shown by analysis of the gases entering and issuing from the tower. In a few years results were obtained which were unexpected by the legislators, for it was found that in very few works was more than 1 per cent. of the HCl produced allowed to escape, whilst beforehand they had lost 15–36 per cent. The losses of HCl from the furnaces and receivers were not included, only those from the chimneys and towers. The law was then revised in 1874, and it was laid down that the fumes from the chimneys of works (by which the gases from the condensing towers were carried away) might not contain more than 0·5 grm. of HCl per cubic metre of gas. It has been shown that in the English works to-day the escaping gases do not contain more than at most 0·2 grm. of HCl per cubic metre. In England, in 1893, 1173 chemical works were being controlled.

In Germany, on the contrary, no law regulating this industry exists, as the manufacturers built their plants more rationally and were interested in utilising the HCl as far as possible. In actual fact the HCl represents a value which alone permits many Leblanc soda-works to exist in face of the competition of the Solvay establishments.

direction to the gases coming from the furnaces.[1] Figs. 60 and 61 show a couple of receivers as commonly employed. They are made of acid-resisting stoneware, and the tubes uniting them one with another are entirely of the same material and are composed of several superposed pieces with rims holding sufficient water to form a hydraulic seal. For the absorption use is also made nowadays of stone towers with tarred walls, and filled with coke, layers of perforated earthenware discs, or earthenware balls. A spray of water falls from the top of the tower, dissolves the acid which ascends from the base, and collects at the base after absorption, being led from there into the receivers. The form of the receivers has also been much modified of recent years, the form which has given the best results having been proposed by Cellarius in 1897 and perfected by Th. Meyer in 1901 (Fig. 62), and constructed entirely in stoneware; this form gives the maximum cooling and absorbing effect with the minimum quantity of water, because its arched shape allows of the largest water surface. It is 80 cms. long, 50 cms. broad, and 30 cms. high, and contains 25 litres of liquid and 45 litres of gas. On the internal arch there is a stoneware ridge or crest (shown in black in the longitudinal section) a few centimetres high and extending along about two-thirds of the length of the receiver (Fig. 63); this forces the water which enters at *a* to traverse the full length of the receiver and back again to the outlet, *b*, along the other side, passing over the point where the crest is lacking; the liquid passes from one absorber to the next through wide glass tubes fixed with mastic


FIG. 61.

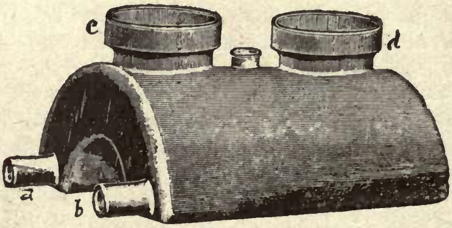


FIG. 62.

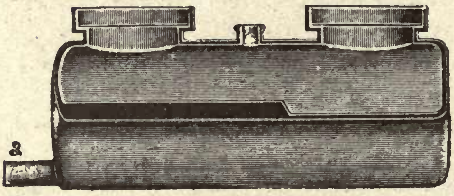


FIG. 63.

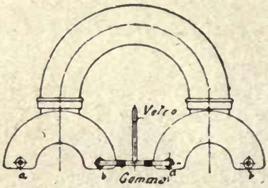


FIG. 64.

---

[1] The concentration of the aqueous solution of the hydrochloric acid collected in the condensation batteries depends on the concentration of the gases and on the temperature of the absorbing water. The following table was prepared by Th. Meyer:

Temperature of the Absorbing Water	Concentration of the Gas						
	5%	10%	20%	30%	50%	70%	90%
	Maximum Concentration of the Resulting Solution (% HCl.)						
5°	33·8	36·1	38·6	40·0	41·9	43·2	44·1
10°	33·2	35·5	38·0	39·4	41·3	42·5	43·4
15°	32·6	34·9	37·3	38·7	40·6	41·8	42·7
20°	32·0	34·2	36·6	38·0	39·9	41·1	42·0
25°	31·3	33·6	35·9	37·4	39·2	40·4	41·3
30°	30·4	32·9	35·2	36·5	38·4	39·6	40·6
40°	29·2	31·5	33·8	35·1	37·0	38·1	39·0
50°	28·0	30·0	32·2	33·6	35·4	36·5	37·4

alternately to the orifices *a*, *b*. The HCl gas enters and issues by the openings *c* and *d*, thus passing over the surface of the water. These vessels, which have a surface of 1 sq. metre, are united with one another by curved tubes as shown in Fig. 64, and are kept cool by immersion two by two in vessels in which water circulates; in this manner each jar has the same efficiency as two or even three of the old type of receiver. In order to cool the gas which issues from the furnace, before it enters the absorption battery it is passed through a battery of empty coolers, shaped, according to Uebel, like inverted Cellarius receivers, as seen in Fig. 65. Between the cooling and absorbing batteries a tower of finely divided material may be advantageously inserted, in order to filter the gases and free them in great part from the impurities, sulphuric acid, arsenic, iron, and selenium. If little space is available these batteries are formed of superposed jars.

A modification of the Cellarius system with an arrangement of superposed vessels is shown in German patent No. 275,700 (1913).

In the furnaces with direct flame 35 to 40 kilos of coal were used per 100 kilos of Na_2SO_4 (150 kilos of HCl of 20° Bé.); in muffle furnaces without gas producers the coal consumption is rather higher and the production rather lower, but the condensation of the HCl is easier and more complete and the product superior. In certain modern mechanical furnaces the consumption of fuel is lowered to one-half (*see* Soda, Part III).

The *Hargreaves process* for the manufacture of HCl was proposed in 1850, was improved by Robinson, and since 1870 has found industrial application. It is based on the direct action of sulphur dioxide (SO_2) on sodium chloride in presence of steam and atmospheric oxygen: $2NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2HCl$.

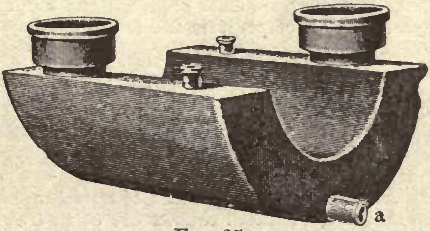


Fig. 65.

This method is advantageous when applied to continuous working on a very large scale. The salt, moistened and compressed into cakes, is introduced into a battery of eight to twelve cast-iron cylinders, 5 metres in diameter and 4 metres high. Below the perforated false bottom of these cylinders sulphur dioxide from pyrites burners enters, mixed with air and steam in the proportion of 2 vols. SO_2, 2 vols. H_2O, and 1 vol. O, and is utilised completely by passing through all the cylinders in succession. During this reaction heat is developed, but on starting fuel must be used to raise the temperature to 500°, after which the temperature is maintained constant and the operation becomes continuous. A notable amount of fuel is thus saved, and sodium sulphate and HCl are manufactured without the need for sulphuric acid, and therefore without lead chambers.[1] It is necessary to work with

---

[1] **Thermochemistry of the formation of HCl and Na_2SO_4 by the Hargreaves process**: To produce SO_2, firstly we have $2FeS_2 + 11\,O = Fe_2O_3 + 4SO_2 + 419{\cdot}8$ cals.—in detail the dissociation of $2FeS_2$ requires 57·6 cals., the formation of Fe_2O_3 evolves 191 cals., and that of $4SO_2$ gives $71{\cdot}6 \times 4 = 286{\cdot}4$ cals. (thus $191 + 286{\cdot}4 - 57{\cdot}6 = 419{\cdot}8$); the quantity of heat corresponding with one molecule of SO_2 is thus $\frac{419{\cdot}8}{4} = 104{\cdot}95$ cals.

In the production of sodium sulphate we have, on the one hand, the heat absorbed by dissociation, from which must be subtracted the heat produced, as shown on the right side of the equation:

$$\begin{array}{lllll} 2NaCl + & H_2O + & O + SO_2 = & Na_2SO_4 + & 2HCl \\ \underbrace{2 \times 97{\cdot}3}_{\text{Cals. } 194{\cdot}6} & 59 & 71{\cdot}6 & 326{\cdot}4 & \underbrace{2 \times 22}_{44} \end{array}$$

Thus the heat evolved by this reaction is:

$$(326{\cdot}4 + 44) - (194{\cdot}6 + 59 + 71{\cdot}6) = 45{\cdot}20 \text{ cals.},$$

which when added to the preceding 104·95 gives a total of 150·15 cals. We must now consider the heat lost by the hot gases remaining after this reaction (which include nitrogen from the air) and by the water vapour; we find, on calculating the amounts, but with reference to 1000 large quantities of salt; every charge requires up to forty tons of NaCl. In order to prevent salt from remaining unattacked in the interior of the cakes it is mixed with coal or sawdust, which then burns and leaves a more porous mass.

This process was tried unsuccessfully in Sardinia, but is much used in England and France, and has been used in Germany in two establishments of the Rhenania Company.

In the Solvay process of manufacturing soda from NaCl, carbon dioxide and ammonia, all the chlorine of the NaCl is converted into ammonium chloride (NH_4Cl). This is then decomposed with lime, which liberates ammonia and forms calcium chloride ($CaCl_2$) in large quantity. In 1878 and 1885 Solvay tried to prepare HCl by treating $CaCl_2$ with silica (SiO_2, kieselguhr, clay rich in silica, etc.), and superheated steam:

$$SiO_2 + CaCl_2 + H_2O = CaSiO_3 \text{ (calcium silicate)} + 2\,HCl.$$

According to Lunge up to 65 per cent. of the theoretical quantity of HCl may be obtained in this way, but this process has not yet had any important application; the same is the case with the use of hydrofluosilicic acid proposed in 1907 by Schollmeyer (German patent No. 191,830). All the same, it is probable that in the near future the $CaCl_2$ from the soda-works will all be utilised for the production of HCl, by means of either silica or magnesia.[1]

---

grms. of sodium sulphate produced and taking the specific heats of the gases into account, that per degree of temperature the following amounts of heat are lost:

513·38 grms. HCl × 0·1845 (sp. ht.) = 94·7 cals.
80·64 ,, O × 0·2175 (,,) = 17·5 ,,
1681·54 ,, N × 0·2317 (,,) = 389·6 ,,
73·24 ,, vap. H_2O × 0·4805 (,,) = 35·2 ,,
Total . . 537·0 cals.

As these gases emerge at a temperature of about 500°, we must multiply this value by 500, so that 268,500 small calories are carried away by them per 1000 grms. of Na_2SO_4, or 38,127 per grm. molecule (142 grms.), corresponding with 38·1 Cals. (large Calories). Furthermore, the heat which is lost on removing the sodium sulphate of specific heat 0·254 from the chambers at 650° will be, for each grm. molecule, $142 \times 0{\cdot}254 \times 650 = 23{,}440$ cals., that is, 23·44 Cals. Therefore the complete loss in the products of reaction will be $38{\cdot}1 + 23{\cdot}44 = 61{\cdot}54$ Cals. Thus the heat available in the complete reaction of the Hargreaves process will be $150{\cdot}15 - 61{\cdot}54 = 88{\cdot}61$ Cals.

It will thus be seen that, if the apparatus is well insulated, once the process is started it will not be necessary to supply heat, and in certain cases it will even be necessary to cool the mass to prevent fusion of the salt (at 772°) and of the sulphate (at 860°).

[1] The method suggested by Lorenz in 1894 and 1897 attracted for some time a certain amount of interest, but has not yet been practically adopted; he proposed to utilise and transform into HCl the extraordinary and excessive quantities of chlorine from the electrolytic alkali works, as the quantity of HCl from Leblanc soda-works is diminishing greatly on account of the rise of the Solvay process.

Lorenz states that by passing a current of steam and chlorine over barely red-hot carbon the chlorine is quantitatively converted into HCl, a mixture of CO_2 and CO being formed at the same time (the CO being more or less abundant according to the thickness of the layer of carbon traversed by the gases); this mixture can be used as a source of energy for heating the apparatus, and the process then continues without requiring further fuel, as the reaction develops heat: $2Cl_2 + 2H_2O + C = 4HCl + CO_2$; one portion of the CO_2 is reduced by carbon, but is again burnt and so made use of: $CO_2 + C = 2CO$ and $CO + O = CO_2$. Experiments carried out by A. Naumann in 1897 showed that the reaction is not quantitative, and up to the present it has not acquired practical importance.

Again, with the intention of utilising chlorine, endeavours have been made to prepare HCl and sulphuric acid simultaneously by passing a current of SO_2 and Cl up a tower filled with stones down which a spray of water passes (or of concentrated HCl in order not to raise the temperature); heat was disengaged and a yield of 65 to 80 per cent. was obtained (Ger. Pat. 157,044 of 1903):

$$2Cl + SO_2 + 2H_2O = H_2SO_4 + 2HCl.$$

This process had already been patented by W. Haner in 1854, was modified by Macfarlane in 1864, and patented, with various improvements, by Deacon in 1868; the last patent but one was that of W. Masson in France in 1892. In 1904 (German patents Nos. 157,043 and 157,044) the Consortium für Elektrochemische Industrie patented a special arrangement of towers, down which conc. HCl passed while $Cl + SO_2$ entered at the bottom; thus 70 per cent. H_2SO_4 (+ 0·6

Attempts have also been made to prepare HCl from the enormous quantities of magnesium chloride ($MgCl_2$) at Stassfurt, by heating it to an elevated temperature with more or less steam, thus obtaining a mixture of HCl + Cl + MgO. The HCl so obtained is condensed in towers and is very pure, as it contains neither sulphuric acid nor arsenic. The method appears to have been introduced at Neu Stassfurt with satisfactory results. The yields are increased by adding boric acid and alkaline-earth or magnesium phosphates and heating the liquid under pressure at 200°; the whole of the hydrogen chloride is then evolved (German patents Nos. 203,080 and 223,169 of 1908).

In the Solvay process ammonium chloride vapours may be passed over red-hot MgO, $MgCl_2$ and NH_3 being obtained. On then heating $MgCl_2$ in a current of steam HCl is formed and the original magnesium oxide recovered: $MgCl_2 + H_2O = MgO + 2HCl$. J. Th. Schlösing (Fr. Pats. 360,356 of 1905 and 394,037 of 1908) heated a concentrated solution of $MgCl_2$ until this showed a boiling-point of 132°, then added a quantity of magnesia corresponding with one-third of the magnesium present as chloride, stirred the viscous mass and dried it at 200°, and then decomposed it in a pan over which hot furnace gases were passed, condensing the hydrochloric acid in the usual manner.

SYNTHETIC HYDROCHLORIC ACID. In the electrolytic preparation of caustic soda, each molecule of sodium chloride yields an atom of chlorine and one of hydrogen, these being the proportions of the two elements in hydrochloric acid. When the problem of the utilisation of chlorine became urgent, the manufacture of synthetic hydrochloric acid was attempted and, ten years or so ago, various works succeeded, after numerous trials, in preparing large quantities of this acid in a very pure state. A hydrogen flame which burned in chlorine was obtained (J. L. Roberts, German patent No. 194,942 of 1905), the two gases being supplied from separate gasometers into a single tube. The condensation is effected by means of pure water in the ordinary earthenware apparatus, and the only impurity of this acid is a little iron derived from the earthenware.

In 1910 the Società elettrochimica di Bussi (Aquila) produced 95 tons, and in 1911 700 tons of the synthetic acid. The Roberts process was employed in America first by the Niagara Alkali Co.

PURIFICATION OF THE CRUDE COMMERCIAL ACID. The commercial acid contains various impurities, especially arsenic chloride, ferric chloride, Cl, SO_2, H_2SO_4, and oxides of nitrogen derived from the ordinary impurities of the H_2SO_4 employed, and also from the NaCl. The ferric chloride turns the acid yellowish, as do also traces of selenium, tellurium, and organic substances.

The purification of the crude acid is complicated and difficult:

To remove ferric chloride the acid is diluted till its specific gravity is 1·145, and then distilled. Fuming hydrochloric acid (36 to 38 per cent. HCl) is first obtained, and then a weaker acid. The ferric chloride distils only with the last portions, which are collected separately, or may be fixed by adding phosphoric acid or calcium phosphate before distillation. Cl and SO_2 are eliminated by discarding the first portion of the distillate. The presence of chlorine in the hydrogen chloride from the ordinary furnaces may be avoided by adding a little powdered wood charcoal with the salt.

The elimination of arsenic is most difficult; the acid is first treated with MnO_2 to oxidise the SO_2, then diluted with water and left in contact with bright copper sheets for some days, after which it is distilled in presence of copper, but the distillate often still contains traces of arsenic.

---

per cent. HCl) collected at the bottom, while the HCl issuing from the top was condensed as usual and the small amount of chlorine in it removed.

In 1909 Coppadoro studied the conditions necessary for a maximum yield and for facilitating the separation of the sulphuric and hydrochloric acids, but the process does not appear to have been sufficiently developed for practical purposes.

The preparation of HCl has also recently been proposed by distilling wood at 300° in presence of chlorine, with a yield of 70 per cent. together with the usual products of wood distillation (Ger. Pat. No. 158,086).

If the acid is distilled in presence of ferrous chloride, $FeCl_2$, the arsenic passes over with the first portions and fairly pure HCl can be obtained. It is often purified by first separating the arsenic from the dilute acid with hydrogen sulphide or barium sulphide (which removes both As_2S_3 and H_2SO_4) and then distilling from glass retorts.

SPECIFIC GRAVITY OF SOLUTIONS OF HYDROCHLORIC ACID AT THE TEMPERATURE OF 15°

Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuum)	Degree Baumé	100 parts by weight of pure aqueous solution of the acid contain:		One litre contains grms. of HCl.
		HCl per cent.	Per cent. by weight of acid of 20° Bé.	
1·000	0·0	0·16	0·49	16
1·005	0·7	1·15	3·58	12
1·010	1·4	2·14	6·66	22
1·015	2·1	3·12	9·71	32
1·020	2·7	4·13	12·86	42
1·025	3·4	5·15	16·04	53
1·030	4·1	6·15	19·16	64
1·035	4·7	7·15	22·27	74
1·040	5·4	8·16	25·42	85
1·045	6·0	9·16	28·53	96
1·050	6·7	10·17	31·68	107
1·055	7·4	11·18	34·82	118
1·060	8·0	12·19	37·97	129
1·065	8·7	13·19	41·09	141
1·070	9·4	14·17	44·14	152
1·075	10·0	15·16	47·22	163
1·080	10·6	16·15	50·31	174
1·085	11·2	17·13	53·36	186
1·090	11·9	18·11	56·41	197
1·095	12·4	19·06	59·37	209
1·100	13·0	20·01	62·33	220
1·105	13·6	20·97	65·32	232
1·110	14·2	21·92	68·28	243
1·115	14·9	22·86	71·21	255
1·120	15·4	23·82	74·20	267
1·125	16·0	24·78	77·19	278
1·130	16·5	25·75	80·21	291
1·135	17·1	26·70	83·18	303
1·140	17·7	27·66	86·17	315
1·1425	18·0	28·14	87·66	322
1·145	18·3	28·61	89·13	328
1·150	18·8	29·57	92·11	340
1·152	19·0	29·95	93·30	345
1·155	19·3	30·55	95·17	353
1·160	19·8	31·52	98·19	366
1·163	20·0	32·10	100·00	373
1·165	20·3	32·49	101·21	379
1·170	20·9	33·46	104·24	392
1·171	21·0	33·65	104·82	394
1·175	21·4	34·42	107·22	404
1·180	22·0	35·39	110·24	418
1·185	22·5	36·31	113·11	430
1·190	23·0	37·23	115·98	443
1·195	23·5	38·16	118·87	456
1·200	24·0	39·11	121·84	469

Better results are obtained by treatment with stannous chloride in scrubbing towers, but the best results appear to be obtained by the recent process (1905) of Messrs. Meister, Lucius, and Bruning in Höchst, who employ vanadous salts which can be obtained cheaply and can be regenerated electrolytically.

According to a recent patent (179,514 of 1907) the arsenic can be separated by bubbling the gas coming from the furnaces through oil; the arsenic is then removed from the oil by washing with water, then with lime, and finally with hydrochloric acid. Harkort patented a process for expelling arsenic by washing the acid vapour in a tower with zinc chloride solution.

The only way of obtaining the purest HCl in the laboratory consists in starting from pure NaCl and pure sulphuric acid and distilling with due precautions.

ANALYSIS OF HYDROCHLORIC ACID. The specific gravity does not always indicate the content of HCl exactly, so that 10 c.c. of the acid (of known specific gravity) are taken, diluted with water to 200 c.c., 10 c.c. of this neutralised with a solution of soda, and the chlorine then titrated with $\frac{N}{10}$ silver nitrate solution, using potassium chromate as indicator. The HCl may also be titrated directly with a normal solution of sodium hydroxide.

The amount of sulphuric acid present as an impurity is determined in 100 c.c. of the solution prepared as above; this is neutralised with soda and precipitated while hot with $BaCl_2$. From the weight of barium sulphate that of the H_2SO_4 is deduced. Iron is determined by reducing with zinc, and, after adding manganese sulphate, titrating with standard potassium permanganate solution. Arsenic is detected qualitatively with Marsh's apparatus (*see later*). Dissolved salts may be determined by evaporation of a definite quantity of the acid to dryness in a platinum capsule.

HYDROBROMIC ACID : HBr

PROPERTIES. This acid was discovered by Balard in 1830. Hydrobromic acid is a gas resembling hydrochloric acid; it fumes in moist air, is 2·8 times heavier than air, can be liquefied at $-73°$ and solidified at $-120°$. It is very soluble in water and the saturated solution at 0° contains 82 per cent. of HBr, and has a specific gravity of 1·78; a solution saturated at 15° contains 50 per cent. of HBr, its specific gravity being 1·51.

On heating this solution, up to 125° a product of almost constant composition distils, of sp. gr. 1·49, containing one molecule of HBr to 5 mols. of water. On saturating HBr solution at $-20°$ with HBr gas, crystals of $HBr, 2H_2O$ separate which melt at $-11°$.

Chlorine displaces bromine from bromides and hydrobromic acid. Hydrobromic acid is less stable than hydrochloric acid and decomposes or dissociates at 800°. The soluble bromides give with silver nitrate a feebly yellowish-white precipitate, not very soluble in ammonia. At a red heat the bromides are more volatile than the chlorides, but less so than the iodides. Hydrobromic acid in aqueous solution is a very energetic acid, and dissolves all those metals which are dissolved by hydrochloric acid, while it dissolves Ag, Cu, Pb, and Hg more readily. A moderately concentrated solution dissolves some sulphides; when still more concentrated it dissolves lead sulphate ($PbSO_4$) very readily, and in presence of amalgamated copper it also dissolves sulphur. A mixture of HBr and HNO_3 behaves like *aqua regia*.

The heat of formation of HBr is 35·2 Kj. (8400 cals.), and on dissolving in 400 parts of water it evolves a further 83·3 Kj. (19,909 cals.). Wood charcoal absorbs much hydrobromic acid evolving up to 64·8 Kj. (15,487 cals.).

USES AND PRICES. Hydrobromic acid is used in the analysis of natural sulphides and in various reactions in organic chemistry. It comes into commerce in 48 per cent.

solution (sp. gr. 1·49) at a price of about 6*s.* 10*d.* per kilo; in 40 per cent. solution (sp. gr. 1·38) it costs 4*s.*, and in 25 per cent. solution (sp. gr. 1·208) 3*s.* 2*d.* per kilo.

PROPERTIES. Bromine does not combine with hydrogen in the cold, even in the light, but combines slowly under the action of heat or of the electric discharge, and more rapidly under the catalytic influence of spongy platinum at high temperatures. Hydrogen gas saturated with bromine vapour burns in the air, giving a cloud of HBr.

Bromine decomposes water in sunlight or in the presence of oxidisable substances such as P, S, Se, and As, producing oxygen (which oxidises these substances) and hydrobromic acid. Various hydrogen compounds, such as H_2S, HI, and NH_3, give HBr with Br.

The method analogous to that used for the preparation of HCl, namely, the action of strong sulphuric acid on bromides, is not of much use for preparing HBr, as the sulphuric acid is partially reduced by the hydrobromic acid, with production of bromine and sulphur dioxide:

$$2HBr + H_2SO_4 = H_2SO_3 + H_2O + Br_2.$$

In presence of water, however, Br is an oxidising agent which is able to convert sulphites into sulphates with formation of HBr:

$$Na_2SO_3 + Br_2 + H_2O = Na_2SO_4 + 2HBr.$$

HBr is more readily formed by the action of dilute sulphuric acid on a bromide in presence of phosphorus.

Hydrobromic acid is easily prepared by dropping bromine on to a paste of one part of red phosphorus with two parts of water; in this way phosphorus tribromide is formed which reacts with water, producing non-volatile phosphorous acid and volatile HBr:

$$3H_2O + PBr_3 = H_3PO_3 + 3HBr.$$

To free the gas thus evolved from bromine vapours which it carries over, it is passed through a tube filled with fragments of glass mixed with moistened red phosphorus. A very regular current of HBr is also obtained by dropping bromine into benzene or crude anthracene: $\underset{\text{benzene}}{C_6H_6} + Br_2 = \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$, and purifying the gas by passing it through a cylinder containing anthracene or paraffin wax.

Hydrobromic acid may also be prepared by the method of Lorenz, which we have already discussed in the case of hydrochloric acid (*see* p. 178): $C + 2Br_2 + 2H_2O = CO_2 + 4HBr$.

When a current of hydrogen sulphide (H_2S) is passed into a flask containing bromine and water, HBr is formed with separation of sulphur: $H_2S + Br_2 = 2HBr + S$. To free this from traces of sulphuric acid, which are also formed, it is distilled in presence of barium bromide, an aqueous solution of pure HBr being thus obtained.

If a current of hydrogen is passed through a flask containing bromine and the gas is then ignited, a considerable quantity of HBr is formed which fumes in the air and shows an acid reaction.

HYDRIODIC ACID: HI

PROPERTIES. Hydriodic acid is a colourless gas which was discovered by Clément and Désormes in 1813; it fumes strongly in moist air, has a specific gravity of 4·4 (air = 1), becomes liquid at − 34° and solid at − 51°. A litre of water at 10° dissolves 450 volumes of HI gas. Light and air decompose the aqueous solution of HI, liberating iodine. The saturated aqueous solution at 0° has a specific gravity of 1·99, and at 126° aqueous HI distils with constant composition ($HI, 5H_2O$) of sp. gr. 1·70 and containing 57 per cent. of HI. Oxygen decomposes hydriodic acid at high temperatures: $2HI + O = H_2O + I_2$. If a flame or a red-hot glass rod is brought to the mouth of a cylinder full of HI gas, the cylinder at once becomes filled with violet iodine vapours. The same result is obtained if an oxidising agent, such as a little hot fuming nitric acid, is introduced into the cylinder. Thus, HI acts as a strong reducing agent, as it easily removes oxygen from oxygenated bodies; it is therefore often employed as a reducing agent in organic chemistry. This acid reacts with silver and mercury even at moderate temperatures, with formation of hydrogen:

$$2HI + Ag_2 = 2AgI + H_2.$$

Chlorine and bromine readily decompose HI:

$$HI + Cl = HCl + I.$$

In 1900 Volhard showed that traces of hydriodic acid are able to act catalytically as an oxidising agent, and to convert considerable quantities of sulphur dioxide into sulphuric acid in presence of water, possibly because free iodine is formed amongst the intermediate products and reacts with the oxidising agent regenerating hydriodic acid:

$$4HI + 3SO_2 + 2H_2O = S + 2H_2SO_4 + 4HI.$$

The I′ ions of iodides give a yellowish precipitate of AgI, insoluble in ammonia, with silver nitrate:

$$AgNO_3 + KI = KNO_3 + AgI.$$

Wood charcoal absorbs much HI gas, developing 92 Kj.

USES AND PRICES. Solutions of HI of 49° Bé. (sp. gr. 1·5) cost 17*s.* 6*d.* to 19*s.* 2*d.* per kilo, and those of 60° Bé. (sp. gr. 1·7) from £1 5*s.* 7*d.* to £1 8*s.* per kilo; they are used, more especially in organic chemistry, as a reducing agent and to introduce iodine into organic compounds.

PREPARATION. Iodine does not combine with hydrogen at the ordinary temperature, even under the influence of light which is chemically very active. At high temperatures it combines only partially, as even at 440° hydriodic acid commences to dissociate into its components. On the other hand, the action is complete if a mixture of hydrogen with iodine vapours is passed over warm platinum sponge, which acts as a catalyser. In this manner pure HI is obtained.

HI cannot be prepared by the action of sulphuric acid on an iodide, as HI, like HBr, readily gives the reverse reaction:

$$2HI + H_2SO_4 = H_2SO_3 + H_2O + I_2.$$

It is, however, readily obtained in abundance by the action of phosphorus tri-iodide on water, in the same way as in the case of HBr:

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

In practice 1 part of red phosphorus is mixed in a flask with 15 parts of water, and 20 parts of powdered iodine are gradually added with constant cooling; the whole is then heated gradually and HI is evolved, which is absorbed by water; this procedure gives an impure product. A better result is obtained by starting with a mixture of 1 part of yellow phosphorus in small pieces with 10 parts of iodine and gradually adding a little water. The HI gas evolved is freed from the iodine, which it carries over, by passing it through a tube containing red phosphorus. If the gas is required it is collected by downward displacement of the air in a dry bottle or cylinder, as it is very heavy and very soluble in water and attacks mercury. By heating the concentrated aqueous solution a regular current of the gas is obtained which can be dried with phosphorus pentoxide.

According to Auger (1909) HI is easily obtained by gently heating to 250° 2 mols. of crystallised phosphoric acid with 1 mol. of KI, and in order to obtain a 56 per cent. solution 2 mols. of phosphoric acid in a 60° Bé. solution are heated with 1 mol. of KI.

A pure aqueous solution of HI is obtained by passing hydrogen sulphide through water containing iodine in suspension until this is decolorised, then heating to drive off the excess of H_2S, filtering from sulphur and finally distilling the HI: $H_2S + I_2 = S + 2HI$.

COMPOUNDS OF THE HALOGENS WITH ONE ANOTHER

These compounds, in common with all compounds of elements which resemble one another closely chemically, have not much stability.

IODINE MONOCHLORIDE : ICl. This is a red crystalline mass which is obtained by the action of excess of dry iodine on chlorine. It is easily decomposed by water: $5ICl + 3H_2O = HIO_3 + 4I + 5HCl$.

IODINE TRICHLORIDE : ICl_3. This compound is formed in presence of excess of chlorine (or from iodic anhydride and phosphorus pentachloride, PCl_5). It forms yellow crystals which yield Cl_2 and ICl at 25°. It dissolves unchanged in a little water.

IODINE BROMIDE : IBr. This is obtained from $I + Br$. It forms crystals similar to iodine which melt at 36°.

IODINE PENTAFLUORIDE : IF_5. This compound shows that iodine may be either tri- or pentavalent. It is formed by the action of iodine on silver fluoride, and is a colourless liquid which fumes in the air.

OXYGEN COMPOUNDS OF THE HALOGENS

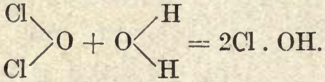
These compounds form with water the corresponding acids, from which the oxides are re-formed when the water is abstracted. They are therefore called *anhydrides* of the respective acids.

Whilst the affinity of the halogens for hydrogen decreases from fluorine towards iodine, their affinity for oxygen decreases from iodine towards fluorine, and whereas iodine and oxygen unite directly, bromine and chlorine combine with oxygen only by means of intermediate products or indirectly. No oxygen compounds of fluorine are known. The more highly oxidised compounds are more stable than those containing less oxygen.

OXYGEN COMPOUNDS OF CHLORINE. The principal oxygen compounds of chlorine are the following:

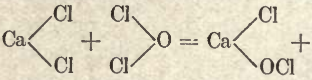
$HOCl$, hypochlorous acid, corresponding with hydrochlorous anhydride, Cl_2O.
($HClO_2$), chlorous acid, not known free, but only as salts.
$HClO_3$, chloric acid, derived from the mixed chlorous-chloric anhydride, Cl_2O_4.
$HClO_4$, perchloric acid, corresponding with the anhydride, Cl_2O_7.

In general from one molecule of anhydride and one molecule of water two molecules of acid are obtained, e. g.,



$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\rangle O + O\left\langle\begin{matrix}H\\H\end{matrix}\right. = 2Cl\,.\,OH.$$

HYPOCHLOROUS ANHYDRIDE (chlorine monoxide = Cl_2O). This compound is obtained by the action of chlorine on precipitated yellow mercuric oxide, *dry* and cooled: $2HgO + 2Cl_2 = HgO,\ HgCl_2 + Cl_2O$. It is evolved as a yellow-brown gas which is condensed in the cold to a red-brown liquid, boiling at + 5°. It is also obtained by dehydrating hypochlorous acid. This compound is very unstable and explosive. It is a powerful oxidising and bleaching agent. When mixed with water it forms hypochlorous acid: $Cl_2O + H_2O = 2HOCl$; with porous calcium chloride it forms chlorine and calcium hypochlorite (chloride of lime):



$$Ca\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right. + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\rangle O = Ca\left\langle\begin{matrix}Cl\\OCl\end{matrix}\right. + Cl_2,$$

and is therefore able to render active the ordinarily inactive chlorine of calcium chloride.

HYPOCHLOROUS ACID : HOCl. This compound is known in aqueous solution only. It is found in chlorine water: $Cl_2 + H_2O \rightleftarrows HCl + HOCl$.

The concentrated solutions of this acid (5 per cent.) are of a yellowish colour and decompose partially on distillation, forming chlorine and chloric acid. Dilute solutions are more resistant to light and are less decomposed on distillation. These solutions have a powerful oxidising and bleaching action on vegetable fibres due to the nascent oxygen which they form. From a given quantity of hypochlorous acid double as much oxygen can be obtained as from the corresponding quantity of chlorine : $Cl_2 + H_2O = 2HCl + O$, whilst, on the other hand, $2HOCl = 2HCl + O_2$; it must, however, be borne in mind that to form 1 mol. of HOCl two atoms of chlorine and 1 mol. of NaOH are required (*see below*).

With HCl the aqueous solutions yield chlorine and water : $HCl + HOCl = H_2O + Cl_2$, and double the amount of chlorine contained in the hypochlorous acid is evolved. When shaken with mercury aqueous solutions of hypochlorous acid form a yellowish-brown precipitate of mercury oxychloride, HgO, $HgCl_2$ (the hypochlorites form HgO). This reaction serves to distinguish hypochlorous acid from chlorine (aqueous), as the latter under the same conditions gives with excess of mercury, mercurous chloride, HgCl (calomel), a white substance insoluble in HCl (Wolters' reaction).

Hypochlorous acid is a weak acid, displaced from its salts even by carbonic acid, which liberates the chlorine.

Pure hypochlorous acid is obtained by the action of chlorine in the dark on freshly precipitated HgO covered with water, with strong agitation (Balard) :

$$2HgO + 2Cl_2 + H_2O = HgO, HgCl_2 + 2HOCl.$$

The whole is then filtered and the liquid distilled; the excess of chlorine is removed by a current of air, a pure aqueous solution of HOCl then remaining.

Hypochlorous acid is also obtained by passing chlorine into water in presence of powdered marble or of an alkali carbonate :

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + CO_2 + 2HOCl \text{ (Williamson)}$$

$$\text{or : } K_2CO_3 + Cl_2 + H_2O = KCl + ClOH + \underset{\text{Potassium bicarbonate.}}{KHCO_3}.$$

If a hydroxide (*e. g.*, NaOH) is used instead of the alkali carbonate, the less active sodium hypochlorite (NaOCl) is formed instead of hypochlorous acid. It is also obtained pure by distilling its salts (hypochlorites) with another weak acid (baric acid), or by acting on a solution of sodium hydroxide with excess of chlorine : $NaOH + Cl_2 = NaCl + HOCl$. In presence of insufficient chlorine sodium hypochlorite is formed.

HYPOCHLORITES AND BLEACHING COMPOUNDS (*see* Part III, Sodium Hypochlorite).

CHLORINE DIOXIDE or **TETROXIDE** : ClO_2 or Cl_2O_4. This was formerly called *hypochloric acid.*

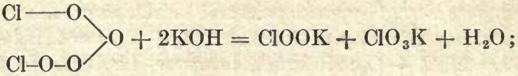
Effront prepared Cl_2O_4 by dropping portions of 5 grms. each of potassium chlorate into a litre of sulphuric acid of 62° Bé. and passing the gas by means of a current of air into a carboy of water, where it was absorbed.

It is formed on treating potassium chlorate with concentrated sulphuric acid in the cold; chloric acid is first formed : $2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3$, this decomposing instantaneously into chlorine tetroxide, water, and perchloric acid (stable) : $3HClO_3 = Cl_2O_4 + HClO_4 + H_2O$.

It is more easily prepared, and with less danger, by treating a mixture of one part of potassium chlorate and 4·5 parts of oxalic acid with sulphuric acid diluted with two volumes of water. When the mixture is gently heated a greenish-yellow gas is formed which liquefies in a freezing mixture.

It is a greenish-yellow gas which in the cold forms a reddish-brown liquid, boiling at 10°, and solidifying at − 79°. If it is pure and free from organic substances it may be distilled on the water-bath at 30°. When exposed to high temperatures it readily explodes. It is therefore always dangerous to treat potassium chlorate with sulphuric acid without taking precautions. To illustrate this violent reaction 3 or 4 grms. of potassium chlorate crystals and a few pieces of white phosphorus are placed in a test-glass full of water; a few drops of strong sulphuric acid are then introduced below the water with a pipette, Green vapours of chlorine tetroxide are at once evolved which set fire to the phosphorus under the water.

The tetroxide dissolves in water with a lemon-yellow coloration, but the solution is decolorised by potassium hydroxide solution, giving salts of cholric and chlorous acids:

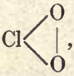
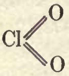


$$\left.\begin{matrix}Cl—O\\ Cl{-}O{-}O\end{matrix}\right> O + 2KOH = ClOOK + ClO_3K + H_2O;$$

hence it behaves as a mixed anhydride of chloric and chlorous acids.

In sunlight the aqueous solution of chlorine tetroxide is decomposed thus:

$$3Cl_2O_4 + 2H_2O = 4HClO_3 + O_2 + Cl_2.$$

Its vapour density corresponds with the formula ClO_2; in this case the chlorine is either divalent,  $Cl\left<\begin{matrix}O\\ |\\ O\end{matrix}\right.$, or tetravalent,  $Cl\left<\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right.$; in solution or in the liquid state the formula is probably Cl_2O_4, *i. e.*, that of a mixed anhydride.

USES. Effront advised the use of aqueous solutions of chlorine tetroxide in the manufacture of spirit from cereals, because ordinarily 20 per cent. of the maize which is treated does not germinate and, according to Effront, by washing these grains with the dilute solution the germination of the grain may be increased by 10 per cent. Experiments made in Sessa's distillery in Milan gave negative results, but in other distilleries the treatment has been used with advantage, especially for damaged maize.

CHLORIC ACID : $HClO_3$. This acid is obtained by decomposing an aqueous solution of barium chlorate with sulphuric acid:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

After filtration the liquid can be concentrated *in vacuo* and a 40 per cent. solution of $HClO_3$ obtained (sp. gr. 1·28).

This solution is oily and decomposes at 40° into Cl, O, and perchloric acid, $HClO_4$; it is thus an energetic oxidising agent, and in this concentrated solution sulphur, alcohol, and paper catch fire.

Chloric acid and the chlorates give free chlorine with concentrated HCl:

$$HClO_3 + 5HCl = 3H_2O + 3Cl_2,$$
$$\text{or: } KClO_3 + 6HCl = 3H_2O + 3Cl_2 + KCl.$$

INDUSTRIAL PREPARATION OF SALTS (CHLORATES) (*see* Part III).

PERCHLORIC ACID : ClO_4H. This is the most stable of the oxygenated chlorine compounds and is formed by the decomposition of chloric acid.

Distillation of 100 grms. of potassium perchlorate with 60 c.c. of 96 per cent. sulphuric acid from a 600 c.c. flask in an oil-bath at 140–190° and under 100 mm. pressure gives perchloric acid, which may be rectified by distillation at 50–65° under reduced pressure; a trace of moisture is allowed to enter during the distillation in order to prevent the formation of crystals of the hydrate, $HClO_4 + H_2O$, in the condenser. The acid thus obtained is of 88–98 per cent. concentration. Perchloric acid may also be obtained by heating its ammonium salt with *aqua regia*.

Mathers (1911) obtained the acid by treating 20 grms. of sodium perchlorate with 30 c.c. of conc. HCl, filtering through asbestos and washing the residual NaCl on the filter with a little HCl and distilling off the latter at 135°; 95 per cent. perchloric acid then remains.

H. Willard (1912) heated 500 grms. of ammonium perchlorate, 600 c.c. of water, and 410 grms. of nitric acid (68–70 per cent.) to boiling, and then slowly added 500 grms. of 8 per cent. hydrochloric acid, the liquid being kept vigorously boiling and the water which evaporates gradually replaced. After the lapse of an hour the mass is distilled, the distillate being discarded until it consists of perchloric acid free from ammonia; the distillate then consists of the hydrate, $HClO_4 + 2H_2O$. Under reduced pressure (200 mm.) a good yield of highly pure acid is obtainable.

When anhydrous it is a colourless liquid of sp. gr. 1·76 (at 22°) which does not solidify even with solid carbon dioxide and ether. It is a strongly corrosive liquid and produces painful wounds on the skin. It reacts violently, with explosion and flame, when mixed with phosphorus, carbon, etc. When kept in the dark and also in the open, it decomposes slowly, and if kept in closed vessels it finally bursts them open. It readily absorbs water.

Lead perchlorate containing an excess of perchloric acid is used as electrolyte in the deposition of lead.

Two hydrates of this acid are known: the monohydrate, $HClO_4 + H_2O$, which at 110° is decomposed forming $HClO_4$, and the dihydrate, $HClO_4 + 2H_2O$, which is a stable oily liquid, of sp. gr. 1·82, distilling unaltered at 203°.

PREPARATION OF PERCHLORATES (*see* Part III).

PERCHLORIC ANHYDRIDE, Cl_2O_7, obtained from the acid by the action of phosphoric anhydride, forms a colourless oil, b.pt. 82°, and undergoes spontaneous decomposition, either slowly or with an explosive flash.

BROMINE and **IODINE** form oxygenated compounds analogous to those of chlorine; there are thus bromates and perbromates, iodates and periodates, etc.

OXYGEN GROUP

This group comprises **Oxygen, Sulphur, Selenium,** and **Tellurium.**

These are divalent elements, that is to say, they combine with two atoms of hydrogen, but only the last three have much chemical and physical analogy with one another; these three are solids, whilst oxygen is a gas which forms compounds analogous in their chemical formulæ only, but not in their properties, as can be seen at once from the following summary:

	O	S	Se	Te
Atomic weight .	16	32	79·2	127·5
Specific gravity .	1·18 (at — 182·5°)	2	4·5	6·4
Melting-point .	— 227°	114·5°	217°	452°
Boiling-point .	— 182·5°	440°	600°	1390°

With increase of the atomic weight, the matter becomes denser; as the density rises the appearance becomes more metallic, but the non-metallic chemical character is preserved. Similar relations have already been encountered in the case of halogens.

At high temperatures these elements all unite with hydrogen, giving compounds of the formula $X''H_2$, but as the temperature rises still further these compounds are dissociated into their components. Oxygen may really be considered as an element apart, as it has very few of the properties common to this group. For instance, oxygen is a gas which, with hydrogen, forms the liquid water, this being non-poisonous and solidifying at 0°; the other elements, on the contrary, are all solid and combine with hydrogen to form gaseous compounds, which are poisonous and difficult to liquefy.

Even from a thermochemical standpoint water differs considerably from the other hydrides, being strongly exothermic, with a heat of formation of 286 Kj., whilst hydrogen sulphide, during its formation from H and S, absorbs 11·67 Kj. Selenium and tellurium also form endothermic compounds with hydrogen.

Aqueous solutions of the hydrogen compounds of S, Se, and Te are decomposed by the oxygen of the air, like hydriodic acid; water, on the contrary, is quite unaltered.

OXYGEN: O, 16

Oxygen exists in three allotropic modifications: (1) active oxygen, composed of free atoms not combined to molecules, chemically very active, and capable of transforming CO into CO_2 in the cold; (2) ordinary oxygen, formed of molecules containing two atoms (O_2), as it is found in the air; (3) ozone, O_3, in which the oxygen has almost the same properties as active oxygen (but is not able to convert CO into CO_2).

Ordinary oxygen was discovered and studied by Scheele in 1771; he prepared it by heating manganese dioxide with sulphuric acid, arsenic acid, or nitric acid, and also from mercuric oxide, etc. It had already been prepared by Hales in 1727, by heating minium, but without having been characterised. At about the same time as Scheele, Priestley independently obtained the gas from saltpetre, but only succeeded in isolating and characterising it in 1774 (in August) when he prepared it by heating mercuric oxide. Bayen also prepared it in 1774 from mercuric oxide.

Condorcet called this gas vital air; the name oxygen was given to it by Lavoisier, on account of its property of forming acids.

According to Duckworth, the Chinese knew oxygen and also the composition of water as early as the eighth century, and, therefore, a long time before Europeans.

Lavoisier predicted the use of oxygen instead of air in order to obtain more rapid and complete combustion in furnaces and for heat production generally in industries, in order to avoid heat losses through the chimneys, through the useless heating of the inert gases (nitrogen) in the air.

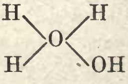
Oxygen is the most abundant and important component of terrestrial matter, being found free in the air (21 per cent. by volume and about 23 per cent. by weight), combined in water (about 89 per cent. by weight), in minerals, in acids, in organic compounds, and in the constituents of animals and plants. In the vital processes of plant assimilation oxygen is set free under the action of sunlight and especially of the rays constituting the spectrum from B to C (red-orange); the minimum development of oxygen is caused by the rays E to *b* (green). Some vegetable cells produce oxygen even without the action of light, for instance, the photometric bacterium and other purple bacteria. The oxygen emanating from plants does not contain ozone, as was believed at one time.

PHYSICAL PROPERTIES OF OXYGEN. Oxygen is a colourless, inodorous gas. Its specific gravity, compared with air, is 1·1056; one litre of oxygen weighs 1·4303 grms. Natterer was not able to liquefy it by pressure alone, even at 1345 atmospheres. In 1877 it was liquefied almost at the same time by Cailletet and by Pictet (*see* p. 29).

The critical temperature of oxygen is — 118° and its critical pressure 50 atmospheres. When liquid, it boils at — 182·5°, at which temperature its specific gravity is 1·118; it is slightly bluish in colour and its heat of evaporation is 51·3 cals. per gram. It solidifies with great difficulty at — 227° on throwing a jet of liquid hydrogen on to liquid oxygen. It then forms a bluish mass, which has a specific gravity of 1·426 at — 252°, and melts at — 219°. Oxygen solidifies with more difficulty than hydrogen or nitrogen owing to its low vapour pressure in the solid state. In 1912 Dewar condensed it on wood charcoal at a very low temperature and found that, with a special vacuum receiver, he could solidify it (in the form of transparent jelly) in a few minutes if the pressure were less than 1 mm. or in twenty minutes at a pressure of 1·15 mm. The solidifying point, namely, 54° abs. (— 219°) agrees with the m.pt., 54·6°, first found by Onnes, and with that derived from the Willard Gibbs vapour pressure formula if the value 1·12 mm. is introduced for the fusion pressure.

The solubility of oxygen in 100 vols. of water is 4·1 vols. at 0° and 2·84 vols. at 20°.

Platinum and silver absorb oxygen when melted, giving it off again during solidification. Four grams of charcoal absorb 105 c.c. of oxygen.

Oxygen is ordinarily divalent, but recent researches and certain organic compounds cause it to be considered as tetravalent in some cases, as though these compounds are derivable from a hypothetical substance, ozonium (dihydrol)  (two molecules of water condensed to one molecule).

CHEMICAL PROPERTIES OF OXYGEN. Oxygen does not itself burn, but supports the combustion of other substances much more energetically than air, as is shown by the following experiments, which also serve to distinguish oxygen from other gases.

(*a*) Combustion in oxygen of a glowing splinter; this catches fire and burns vividly.

(*b*) Combustion in oxygen of a lighted taper; this burns with a bright light, forming CO_2, which renders a solution of barium hydroxide milky.

(*c*) Combustion of lighted sulphur in oxygen; burns with a bright flame and forms SO_2, which reddens blue litmus paper.

(*d*) Combustion of lighted carbon disulphide in oxygen; same as sulphur.

(*e*) Combustion of white phosphorus in oxygen; this melts, catches fire, and burns with a very intense white flame, producing a white powder of P_2O_5.

(*f*) Combustion in oxygen of an iron spiral to which lighted tinder is attached; this burns, forming a shower of sparks and producing brown iron oxide.

(*g*) Combustion of magnesium wire in oxygen; this gives an extraordinarily intense white light.

(*h*) Combustion of an iron wire with a spirit lamp and jet of oxygen; the iron burns vividly with a shower of luminous sparks.

Oxygen combines directly or indirectly with all the elements except fluorine, helium, and argon.

The combination of oxygen with other substances is generally called *combustion* (*see* flameless combustion: chapter on carbon) if accompanied by flame, fire, and light, as shown in the experiments just recorded; if it takes place without production of fire, it is called *oxidation*, *e. g.*, iron oxidises in the air, producing rust, etc.

The temperature of ignition of various substances in oxygen and in air varies greatly; phosphorus ignites at 60°, hydrogen at 580° in air and in oxygen, the vapours of carbon disulphide at 149° in air, moist carbon monoxide at 650° in air and in oxygen, acetylene at 420° in air or oxygen, hydrogen sulphide at 220° in oxygen and at 360° in air, ammonia at 700°–860° in oxygen. In general the temperature of ignition depends also on the velocity of the jet of gas and the nature of the vessel. The temperature of the flame varies with the nature of the burning substance (*see* p. 135).

Substances are known which catch fire spontaneously in the air when in a state of extremely fine division, and these are called *pyrophoric substances;* Pb, Fe, Cu, Ni, P, etc., are easily obtained in this condition. A simple experiment may be performed with pyrophoric lead, which is obtained by thoroughly igniting lead tartrate in a test-tube, wiping the water from the sides of the tube, and then closing it with a rubber stopper. After the lead, which remains in a state of very fine subdivision, has cooled, it is thrown suddenly into the air, when it catches fire with production of sparks and flame.[1]

The ignition of moist hay in ricks [2] and of oily cotton and woollen waste is also due

---

[1] Auer (1903) prepared pyrophoric alloys which produce numerous sparks by gentle friction; a single gram of such a powdered alloy can be used thousands of times for the production of fire, and it has been proposed for many practical applications, such as for fireworks, for kindling gas-jets, firing mines, kindling motor lamps, firing motors, for signalling lamps, etc. These alloys contain rare metals, especially cerium, lanthanum, praseodymium, and neodymium. Ten years ago a few grams cost a considerable sum, but to-day these alloys are sold at £4 16*s.* per kilo, as the price of the rare metals, which are obtained by the electrolysis of their fused chlorides, has diminished. The mixture or alloy with the other metals is prepared by special machinery, but always out of contact with the air, as it easily oxidises or catches fire. The alloys are known as *Auer* metal and are sold in 10-kilo blocks. The pyrophoric character is attributed to the formation of suboxides of the rare metals. The best effects are produced with an alloy containing 70 per cent. of cerium and 30 per cent. of iron, or 10 per cent. of copper, etc.; magnesium produces fewer sparks, so that it is necessary to find out the proportions of each metal which are needed to form a pyrophoric alloy with these rare metals. Some authorities attribute the pyrophoric character to traces of oxides which form on the surface of these metals, whilst others maintain that it is due to the fineness of the particles yielded by the more or less coarsely roughened surface.

[2] According to the results of experiments made by H. Miche (1912) the heating of moist hay is due: (1) up to 40° to *Bacillus coli* or to the respiration of grass still alive; (2) up to 40–75° to *B. Calfactor*; and (3) beyond 75° to purely chemical phenomena. To start the heating at least 25 per cent. of water must be present.

both to the action of special ferments and to the spontaneous oxidation of finely divided oil, with consequent rise of temperature and final ignition; this spontaneous ignition appears to be accelerated by the presence of certain catalytic substances (even finely divided iron). The spontaneous combustion of heaps of coal containing pyrites is also a pyrophoric phenomenon, as the moisture and oxygen of the air sometimes convert the pyrites into $FeSO_4$ and H_2SO_4, and in this way produce so much heat that the coal is ignited. Wool and cotton baled moist may also ignite spontaneously, especially if they contain certain impurities. Finely divided platinum is also able to accelerate the oxidation of many substances. Finely powdered aluminium sometimes catches fire. Fires in coal-mines are due to very fine coal-dust suspended in the air, and similarly spontaneous fires in flour mills may be ascribed to very fine flour-dust in suspension; similar remarks apply to sulphur and sugar refineries. C. Engler (1907) has shown that the danger of explosion in mines or other places where powdered inflammable substances are present is much greater when minimal quantities of inflammable gases, such as firedamp (methane), coal-gas, hydrogen, etc., are also present in the air. When such gases are absent explosion does not easily occur, even with a spark.

Oxidations and all direct combinations of oxygen with other elements occur only in presence of minute quantities of water. If the reagents are absolutely dry no reaction occurs. Dry phosphorus does not burn in dry oxygen, and dry hydrogen appears not to combine with dry oxygen, even with the electric spark. In these cases water may exert a catalytic contact action which initiates the reaction. A mixture of one volume of oxygen with two volumes of hydrogen (detonating gas) produces a strong detonation if fired with a flame, the temperature of ignition being 650°.

By projecting the flame of the oxy-hydrogen blowpipe on to a piece of quicklime, a dazzling light is obtained, known as the Drummond light (lime-light), which is used in lighthouses, for projection lanterns, and for other purposes. The oxy-hydrogen flame (from H and O) melts iron, platinum, etc.

Oxygen is respirable even alone, and revives vitality; it is therefore employed in grave cases of illness when the breathing is hindered and the patient would certainly succumb if it were not possible to meet the needs of the organism by breathing oxygen more concentrated than that present in the air, and so facilitating a more rapid oxidation of the blood. By respiration of purer oxygen the blood acquires a brighter red colour. The oxygen of the air which we breathe transforms venous into arterial blood by its absorption, forming CO_2. Plants also breathe air, but they absorb the carbon dioxide more especially and emit oxygen, so that equilibrium is more or less established in nature between the activities of animals and plants, as the oxygen consumed by animals and by combustion, with production of CO_2, is regenerated by plants, which absorb the carbon of the CO_2 and return free oxygen to the air. For the life of fishes a minimal quantity of oxygen is required.

A. Mosso showed that in oxygen at two atmospheres pressure many animals are able to live even in presence of 6 per cent. of carbon monoxide, which is very poisonous, whilst under ordinary conditions they cannot withstand even one part per thousand. If suddenly removed from such an atmosphere into the outer air these animals quickly died. This fact, studied by Mosso, may have useful application in the case of miners who are the victims of firedamp explosions. Many of these unfortunate people die, even after a week, by slow poisoning, whilst if, after being rescued, they were placed under a bell in oxygen compressed to two atmospheres or air at ten atmospheres they might be saved.

Trials made in 1901 and 1902 appear to have given favourable results, but there are very few indications of subsequent applications.

APPLICATIONS OF OXYGEN. It is used with hydrogen for the fusion and welding of platinum, since the method was perfected by Deville and Debray during their important work on this metal (1852–1857). In spite of its very high melting-point (1770°), they succeeded in melting, welding, and shaping platinum in various ways by means of the oxy-hydrogen blowpipe. In this way they contributed considerably to the progress of certain branches of chemistry and physics, as before that time it was not possible to construct platinum apparatus of complicated form for any purpose; since that time much platinum apparatus has found industrial application. Fig. 66 shows an oxy-hydrogen blowpipe fed by hydrogen and oxygen from two steel cylinders which contain the compressed gases. Oxygen is supplied to the inner and hydrogen to the outer tube of the blowpipe, and the quantity of either can be regulated at will, so that a reducing or oxidising flame can be obtained as required. For autogenous welding of iron a reducing flame is commonly used. For some years the oxy-hydrogen flame has been advantageously replaced by the oxy-acetylene flame, that is to say, the hydrogen has been replaced by acetylene supplied either from a gasometer or from a solution of acetylene in acetone. This has the advantage of yielding a higher temperature, and whilst in a reducing flame about 4 cu. metres of hydrogen are required per cu. metre of oxygen, only 700–800 litres of acetylene are required (*i.e.*, 2·5 kilos of calcium carbide).

With the oxy-acetylene flame large plates of steel can be cut with the greatest facility and precision (armour plates, etc.), and in a few minutes holes of 5–10 cms. diameter can be made in blocks of iron half a metre and more in thickness. The autogenous welding of iron, aluminium, and copper is performed with the greatest ease and perfection.[1]

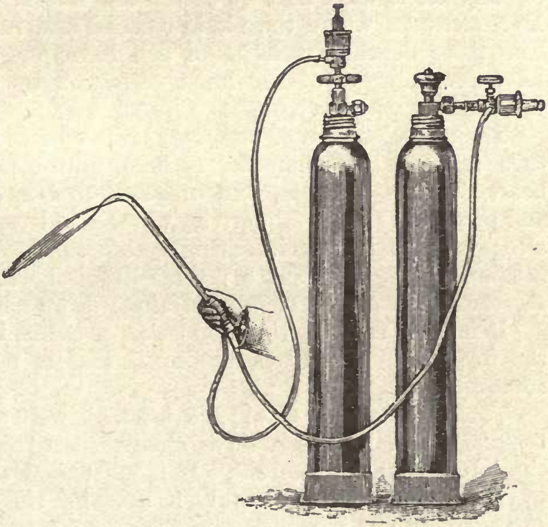


FIG. 66.

The employment of oxygen in combustion in general has a secure future, and trials which have been made in large works have shown very promising results. By its employment the useless heating of enormous quantities of nitrogen, which constitutes four-fifths of the air and enters cold into the furnaces to issue through the chimneys at 250°–350° without having played any part

---

[1] *Oxy-acetylene blowpipe* Whereas the oxy-hydrogen blowpipe usually gives a temperature of about 2100°, the oxy-acetylene blowpipe gives up to 3000°. The latter is best for the autogenous welding of metals, whilst the former is to be preferred for cutting great thicknesses of metal. The only metal which cannot be autogenously welded is nickel, since when melted this metal absorbs gas which produces a continuous projection of particles of fused metal against the blowpipe.

Nowadays greatly improved oxy-acetylene blowpipes are used, the oxygen being supplied under a pressure of 1·5–2·5 atmospheres or, for cutting heavy metal, even at a higher pressure. The oxygen current sucks the acetylene from a gasometer, the tubing from the latter being interrupted at a certain point by a hydraulic safety-valve which prevents communication of the acetylene gasometer with the oxygen in case the flame shoots back. About equal volumes of the two gases are consumed and, when well regulated, the flame has the form of a long, almost colourless or feebly blue spear (15–20 cm.) with a small, shining, white nucleus at the base, 2–4 cms. long. Cuts or holes are made by putting this nucleus in direct contact with the object to be welded or cut. When holes are to be made, as soon as the temperature of liquefaction of the iron is reached, the acetylene (or hydrogen) stream is diminished, while that of oxygen is increased, the iron being thus rapidly oxidised and the liquid oxide thrown to a distance as a shower of sparks. In welding cast-iron, more care is taken, since this melts more easily than the oxide, and in welding aluminium, fluxes (chlorides, borax, or, better, potassium carbonate, etc.) are added to eliminate the oxide, since this does not melt. Copper may be welded, but not cut or pierced, as it is not easy to remove and fuse copper oxide.

in the combustion, is avoided. In order to use oxygen for this purpose furnaces and hearths of special type, more resistant to high temperatures, are required; also the chimneys will be smaller, as smaller quantities of gas are formed.

Trials made in the glass industry with melting furnaces gave good results; better melts were obtained in less time with a saving of 50 per cent. of fuel (Thomas's patent 1886 and 1891).

Oxygen is used in England to purify coal-gas from hydrogen sulphide; Laming's material is revivified by a current of oxygen, which oxidises the ferrous sulphide and separates the sulphur (44 litres of oxygen oxidise 100 grms. of H_2S).

Oxygen is also used to free spirits from fusel oil, and for oxidising oils used in varnish manufacture, and for bleaching.

Divers are able to use oxygen prepared by the action of sodium peroxide on water, the sodium hydroxide which is also formed serving to absorb the expired CO_2 (*see below*).

Oxygen is used also by aeronauts, who sustain themselves by its use at high altitudes where the air is rarefied and respiration needs to be assisted. The more delicate varieties of fish have now been successfully transported alive for journeys of 100 hours' duration by being kept in vessels in communication with oxygen.

The medicinal use of pure oxygen is now widely diffused, as it is of advantage in cases of asphyxia, asthma, auto-intoxication, pulmonary diseases, heart diseases, anæmia, and diabetes, and is of especial use in intensifying and prolonging the vital activity where this is very low and in danger of ceasing altogether; it has a cicatrising action in the cure of wounds and purulent inflammations. In 1897 a private hospital was established in London where treatment by means of oxygen alone is practised.

It may be used for the production of ozone, instead of air, in order to avoid the formation of nitrous products, and is now used for cleaning internal combustion engines.

The various uses of oxygen for high temperature production by burning together with hydrogen have already been discussed under the heading of the latter element (p. 136). It is calculated that about 80 per cent. of the oxygen manufactured in Italy is used for the autogenous welding of metals (wrought- or cast-iron, aluminium, copper) or for cutting or perforating wrought- and cast-iron sheets or blocks.

SALE OF OXYGEN. Oxygen is supplied in cast-steel cylinders at 120 to 130 atmospheres pressure; the cylinders are tested every two years to a pressure of 250 atmospheres; obviously each cylinder contains 130 times its capacity of oxygen at the ordinary pressure. These steel cylinders ordinarily contain 1½, 4½, or 6½ kilos of compressed oxygen, that is, 1, 3, or 6 cu. metres, and the weight, including cylinder, is 12 to 13 kilos per cubic metre of oxygen. A knowledge of these data is necessary in order that the cost of transport of the bomb backwards and forwards may be calculated.

When oxygen is required in the laboratory at lower pressures a pressure-regulator of very simple character is used, consisting of a glass cylinder almost full of mercury closed with a bung fitted with two glass tubes; one of these dips more or less deeply into the mercury and serves as a delivery tube for the oxygen from the cylinder, whilst the other conducts the gas to the apparatus in which it is required.[1] The current of gas can thus be regulated by immersing the tube more or less deeply in the mercury. The pressure regulators used industrially are analogous to those illustrated in the chapter on Liquid Carbon Dioxide.

The price of oxygen in small quantities for the laboratory, for medical use, etc., is about 5*s.* to 6*s.* 8*d.* per 1000 litres, compressed in steel cylinders. The steel cylinder costs

---

[1] *Translator's note.*—It is obvious that by this means the pressure could only be lessened to a very limited extent.

£1 12*s*. to £2 8*s*., according to size, but is lent on hire by the manufacturers. On the large scale 1000 litres of industrial oxygen (containing 2 to 3 per cent. of nitrogen) cost about 2*s*. 6*d*., while for that containing 8 to 12 per cent. N the price is more than 1*s*. 2*d*. in Italy.

Almost all the oxygen is nowadays made by the liquid air process. In 1904–1912 the Linde Company alone made 81 such plants for oxygen (and 22 for nitrogen) for various countries, the capacity being 6,000,000 cu. metres per annum.

According to the official statistics the amount of oxygen produced in Italy was 21,000 cu. metres in 1906 and 29,000 cu. metres in 1907, valued at £5800, and the production should be notably increased, as several new works are being started to produce it from liquid air. Private information received indicates that the Italian production reached 250,000 cu. metres in 1913. In the calcium cyanamide works at Piano d'Orte (*see later*) 300 cu. metres of oxygen can be made daily from liquid air.

In Germany, in 1908, 8000 cu. metres of oxygen were produced by Brin's process, 342,000 electrolytically, and 2,200,000 cu. metres from liquid air. The latter, when for industrial use (98 per cent.) and when used on the spot without compression, costs about 2½*d*. per cu. metre.

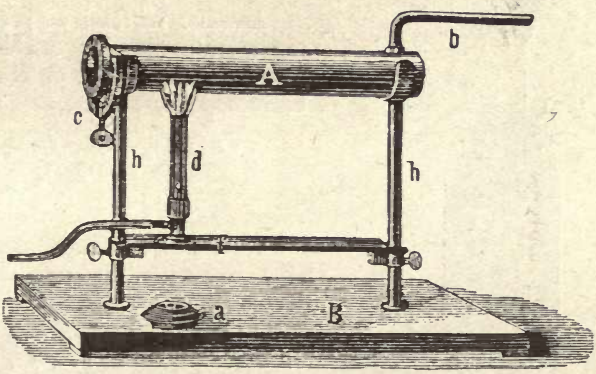


Fig. 67.

For welding metals alone, about 8,500,000 cu. metres of oxygen were used in Germany in 1912, more than 5,000,000 of this amount being from liquid air.

The world's production of oxygen in 1910 was about 10,000,000 cu. metres (147 works), while in 1915 this production was almost doubled. In France the production is about 3,000,000 cu. metres, in England 1,500,000, and a similar amount in the United States. The sale price in France is 1*s*. 3*d*. to 1*s*. 7*d*. per cu. metre compressed in steel cylinders and in Germany 10*d*. to 1*s* 3*d*.

LABORATORY PREPARATION. Apart from the electrolytic decomposition of water (*see* Hydrogen, p. 140) oxygen is commonly obtained by heating potassium chlorate in a retort; the reactions are as follows:

(*a*) $4KClO_3 = KCl + 3KClO_4$; and (*b*) $KClO_4 = KCl + 2O_2$.

The development of oxygen commences when the chlorate is quite fused, that is, above 350°; on heating still further the mass swells up and the gas evolution becomes copious and almost tumultuous.

By adding a small quantity of the following oxides a regular gas evolution is produced at a lower temperature:

Oxides added	Fe_2O_3	MnO_2	CuO	Platinum black	PbO_2
O developed at	120°	205°	235°	270°	285°

The first three oxides also cause spontaneous heating of the mass during the reaction. Addition of NaCl or KCl retards the reaction and renders it more regular (12 parts of $KClO_3$, 6 parts NaCl, 1 part MnO_2).

When the above-mentioned oxides are employed the oxygen obtained contains small traces of chlorine, and also of CO_2 if the chlorate is impure. The chlorine is eliminated by washing the oxygen with a solution of NaOH, or by suspending a little bag of copper hydroxide in the gasholder.

The preparation of oxygen from $KClO_3$ by inexpert operators has often led to terrible explosions and loss of life. Admixture with the chlorate of small pieces of organic rubbish (paper, fibres, wood, etc.) may cause fatal explosions. The same thing may happen if the tube in which the gas is developed is too narrow. In the laboratory use is often made, for heating the mixture, of a cylindrical iron tube, *A*, closed with a screw cover (Fig. 67), and with a wide delivery tube, *b*. The front portion of the tube, near the delivery tube, is first heated and the flame then gradually moved to the other extremity, *c*. With this apparatus large quantities of oxygen can be prepared without danger.

The oxygen evolved is washed in Woulff's bottles with NaOH solution, and is then collected in a gasholder by displacement of the water by entry through the lower opening, *B*, by means of the tube *G* (Fig. 68). As the gas enters the same volume of water escapes. When the gasholder is full the opening, *B*, is closed with a stopper, and when oxygen is required it is withdrawn from the tube *R*, provided with a tap, and is replaced in the gasometer by water from the funnel, *T*, through the tap, *H'*, and the long tube reaching to the bottom of the gasometer. Such gasholders of glass or metal are very useful in any case in which a gas is to be collected by displacement of water.

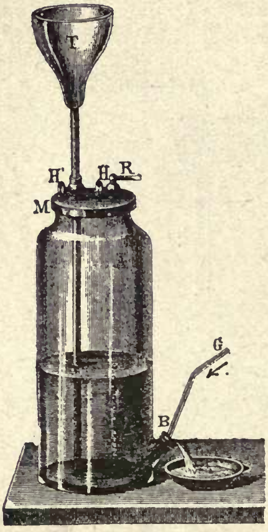


FIG. 68.

Another method of preparing oxygen is by heating certain metallic oxides such as mercuric oxide: $2HgO = 2Hg + O_2$, or the peroxides of manganese, barium, lead, etc.

$$3MnO_2 = Mn_3O_4 + O_2 \text{ (at a red heat).}$$
$$3PbO_2 = Pb_3O_4 + O_2.$$
$$BaO_2 = BaO + O \text{ (industrial method).}$$

Webster's method consists in heating various potassium oxy-salts, for example, potassium nitrate, which yields oxygen and potassium nitrite: $KNO_3 = KNO_2 + O$. If the temperature is too high nitrogen is also formed: $2KNO_2 = K_2O + N_2 + 3O$; by the addition of a little ZnO the reaction can be made to take place at a lower temperature. The development of oxygen by this reaction can be shown by throwing a small piece of lighted carbon on to the surface of fused potassium nitrate in a capsule; the carbon immediately burns away rapidly in contact with the nascent oxygen which is evolved.

Pure oxygen is obtained by heating potassium permanganate gently: $4KMnO_4 = 2K_2MnO_4 + Mn_2O_3 + O_5$.

Oxygen may be prepared, as Scheele suggested, by heating MnO_2 with sulphuric acid or with sodium bisulphate, $NaHSO_4$, as this does not destroy the retort at a dull red heat:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

If, however, these reagents contain chlorides the oxygen will be mixed with chlorine. MnO_2 may also be heated with silica, when it forms oxygen and manganese silicate: $MnO_2 + SiO_2 = MnSiO_3 + O$.

A very regular development of pure oxygen is obtained by heating in a retort 3 parts of potassium dichromate and 4 parts of strong sulphuric acid:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Oxygen can be prepared at the ordinary temperature from a mixture of 3 mols. of BaO_2 and 1 mol. of $K_2Cr_2O_7$ with dilute sulphuric acid, or a mixture of equal parts of barium and lead peroxides (BaO_2 and PbO_2) with dilute nitric acid may be employed. In both these cases hydrogen peroxide (H_2O_2) is first formed and yields oxygen in contact with the oxide of chromium or lead. Cubes made of a paste of 2 parts of BaO_2 and 1 part of gypsum are very useful as they can be employed in a Kipp apparatus with dilute HCl (Neumann, 1887). In this case the oxygen contains chlorine, and explosions often occur.

Instead of BaO_2 Volhard proposes the use of chloride of lime, $CaOCl_2$, with hydrogen peroxide acidified with sufficient HCl or HNO_3 to neutralise all the lime :

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

He uses 300 grms. of $CaOCl_2$ (showing 35 per cent. Cl), 1 litre of H_2O_2 (of 3 per cent. O) and 73 c.c. HNO_3 of sp. gr. 1·36 or 57 c.c. HCl of sp. gr. 1·17. Oxygen is obtained from calcium hypochlorite in the cold by a mixture of iron sulphate and copper sulphate, which acts as a catalyser (Jaubert, 1903) : to 70 parts of chloride of lime and 350 parts of water is slowly added a solution of 12 parts of ferrous sulphate and 3 of copper sulphate in 50 parts of water.[1]

Also 100 c.c. of hydrogen peroxide (3 per cent.), made alkaline with ammonia, develop 1 litre of oxygen in the cold when treated with a dilute (0·3 per cent.) solution of potassium permanganate. Hydrogen peroxide, made alkaline with caustic potash, readily develops oxygen with a solution of potassium ferricyanide, which is converted into the ferrocyanide :

$$\underset{\text{58 grms.}}{2Fe(CN)_6K_3} + 2KOH + \underset{\text{100 c.c.}}{H_2O_2} = 2Fe(CN)_6K_4 + 2H_2O + \underset{\text{2 litres.}}{O_2} \text{ (Kassner's method).}$$

Instead of H_2O_2 one may also employ BaO_2 in this process. In both these cases we have an apparently paradoxical result, namely, the reduction of the ferricyanide by an oxidising agent.

Sulphuric acid, in common with some sulphates, such as zinc sulphate, decomposes as follows when thrown on to a red-hot plate : $H_2SO_4 = SO_2 + H_2O + O$; by passing the gases through water and KOH solution the SO_2 is absorbed and free oxygen obtained (Debray and Deville). By the action of chlorine on steam at 120°, we have : $Cl_2 + H_2O = 2HCl + O_2$.

Mallet transforms Cu_2Cl_2 with steam at 100° to 200° into $CuOCl_2$, which gives $Cu_2Cl_2 + O$ at 400°; this process was applied on a large scale, but afterwards abandoned. Industrially oxygen is prepared by the electrolysis of water, either acidified or made alkaline, as we have seen when considering hydrogen.

We give below a summary of the yields of oxygen prepared by various chemical methods :

1 kilo	$KClO_3$	produces	274	litres O,	100 litres	costing	$7\frac{1}{4}$*d.*
,,	$MnO_2 + H_2SO_4 + H_2O_2$	,,	129	,,	,,	,,	4*s.* 5*d.*
,,	MnO_2 (at red heat)	,,	86	,,			
,,	H_2SO_4	,,	114	,,			
,,	$ZnSO_4$	,,	39	,,			
,,	$NaNO_3$	,,	329	,,			
,,	$CaOCl_2$ (35%) + H_2O_2	,,	52	,,	,,	,,	4*s.* 10*d.*
,,	BaO_2, theoretically (but practically one-half)	,,	120	,,			

PHYSICAL METHODS OF PREPARING OXYGEN. Mallet based a method on the property of water of dissolving more of the oxygen than of the nitrogen of the atmosphere, so that by liberating the gas and absorbing it anew it is continually enriched in oxygen, and after the operation has been repeated four times contains 75 per cent. Helouis improved this method by employing a 20 per cent. solution of glycerine instead of water.

By repeated passages through a sheet of india-rubber air can be enriched in oxygen up to 90 per cent. (Graham, Margis, etc.). This is a phenomenon, not of diffusion, but of osmosis, in which the principal influence is exerted by the osmotic action of the membrane, this allowing the oxygen to pass more readily than the nitrogen in spite of its slower

---

[1] By investigating the velocity of development of oxygen from chloride of lime in presence of small quantities of cobalt nitrate, M. Bell (1913) showed that concentrated solutions of the nitrate cause evolution of chlorine, whilst very dilute solutions (less than 0·005-normal) cause development of oxygen at about 180°. The velocity of the evolution is proportional to the concentration of the components and increases rapidly with rise of temperature. Alkalis retard the reaction, as also do LiCl, Na_2CO_3, Na_2S, $KMnO_4$, $SnCl_2$, and KNO_2, whereas acceleration is caused by acids or by $CuSO_4$, $AgNO_3$, KCN, $HgCl_2$, $FeCl_3$, $K_2Cr_2O_7$, and $FeSO_4$; salts of Cu, Ag, Fe, and Ni, when concentrated, cause liberation of chlorine.

molecular movement. A silver tube heated to 600° forms an osmotic diaphragm which permits of the passage of oxygen, but not that of nitrogen (Aumont and G.Deville d'Avray: French patent No. 451,307 of 1912).

Montmagnon, de Laire, and A. Schmidt prepared oxygen by making use of the fact that charcoal absorbs more oxygen than nitrogen from the air.

On the large scale oxygen is prepared by liquefying air and then allowing the nitrogen to evaporate (*see below*).

Oxygen is paramagnetic, that is to say, it is attracted by a magnet, whilst nitrogen is magnetically inactive; this property of the former gas is especially evident in the liquid state, so that the proposal has been made to separate the oxygen from the nitrogen of the air by a centrifugal machine in presence of a magnet; the oxygen is also the denser of the two liquids, and separates as a distinct layer; the process is not of practical use.

INDUSTRIAL METHODS OF PREPARING OXYGEN. The largest quantities are produced by the physical methods just discussed.

The chemical method which has been most successful up to the present is that of the brothers Brin (formerly Brin's Oxygen Company, London), which is based on reactions discovered by Boussingault: On heating barium oxide, BaO, in porcelain tubes to 500° in a current of air, free from CO_2, it forms barium peroxide, BaO_2, and at a temperature of 800° this is again split up into BaO + O. On now lowering the temperature again to 500° the regenerated barium oxide absorbs further oxygen from the air with formation of the peroxide, which again gives up this oxygen at 800°; 100 grms. of BaO yield in this way 5–6 litres of oxygen. This method is interesting on account of the continuous regeneration of the intermediate product, BaO_2, without any loss of secondary products.

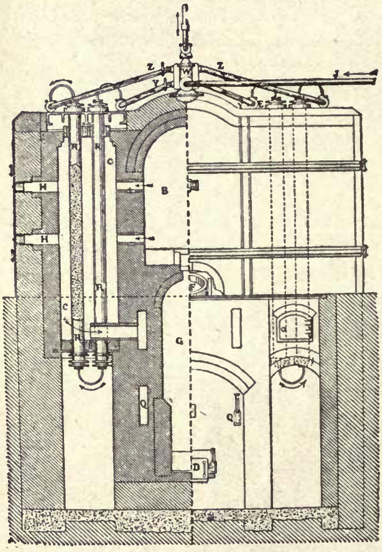


FIG. 69.

In practice, however, many difficulties were encountered, the most serious being the fact that the barium oxide was found gradually to lose its power of absorbing oxygen and had therefore to be often renewed.

In 1868 Gondolo tried to avoid this inactivity of the BaO by adding CaO,MgO, potassium permanganate, etc., but all proved useless. The true reason why the BaO became inactive was not discovered till much later. In 1881 the brothers Brin discovered that in order to keep the BaO active it was necessary to employ dry air, free from CO_2 and organic substances, and generally from substances capable of yielding CO_2 on combustion, as otherwise barium carbonate, $BaCO_3$, is formed, and with water barium hydroxide, $Ba(OH)_2$, which are inactive products, and are decomposed only at much more elevated temperatures.

In 1883 the brothers Brin took out a patent for this method (Ger. Pats. 15,298 and 59,132), and after various improvements they applied it industrially in England and Germany. The air is purified by passing through sodium hydroxide solution or granulated sodium hydroxide, the sodium carbonate which is formed being otherwise utilised; it is then dried with quicklime, after which it enters cylindrical, vertical, cast-iron retorts, *R*, contained in a furnace, *C* (Fig. 69). The retorts contain hard porous BaO, obtained by heating barium nitrate to 880°: $Ba(NO_3)_2 = BaO + O_2 + N_2O_3$, the yield being 50 per cent. by weight of the nitrate; the BaO costs about £80 per ton (*see* other methods of preparation in the chapter on Barium Nitrate, Part III). The temperature of the BaO in the retort is kept at about 550° by means of the producer, *G*, the hot gases from which enter through *B* into the space, *C*, surrounding the retorts. The air is under a pressure of 1½ atmospheres, the absorption of oxygen being thus hastened. The air is then shut off, the temperature raised to 700°, and the retorts evacuated to a pressure of 5 cms. of mercury. *In vacuo* the oxygen is given off more easily and at a lower temperature (700° instead of 800°). The air which enters through the tubes *J* and *Y* has to pass through the whole length of BaO in the long retorts, and when the temperature has been raised to 700° the evolved oxygen is led to the gasometers by the tube *Z*.

Each operation lasts about fifteen minutes, and the yield is about 10 litres of oxygen per kilo of BaO. At one time as much as 40 litres of oxygen per kilo of BaO were obtained, but the operation lasted two hours; now the yield is apparently less, but in reality very much more is obtained per unit of time, the cost remaining the same.

The Brin process was improved in 1900 by increasing the useful life of the BaO by depositing it in thin layers on the surface of inert materials in a finely divided state; it then lasts as long as forty days without diminution of the yield.

Oxygen prepared in this manner contains 90 per cent. of O and 10 per cent. of N, and costs 2–2·5*d.* per cu. metre altogether, including sinking fund, fuel, power, etc., but excluding the compression into steel cylinders. Nowadays, however, the Brin process has been replaced almost everywhere (including England) by the liquid air process, which is becoming of more importance than all the others, and will be discussed in detail further on in the chapter on Liquid Air.

To obtain pure oxygen industrially, for the laboratory and for medical use, free from carbon monoxide and dioxide and from hydrocarbons, Dutremblay and Lugan revived in 1897–1899 a method of Tessié du Motay, proposed in 1867 and afterwards forgotten. This consists in the decomposition of sodium permanganate in numerous vertical retorts (14 cms. in diameter and 2·40 metres high) which are heated to 500° in a furnace and evacuated in presence of superheated steam. The first phase of the reaction is:

$$Na_2MnO_4 + H_2O = 2NaOH + MnO_2 + O;$$

the oxygen is then washed with cold alkali solution and collected in gasometers. In the second phase the manganate is regenerated by passing through the retort a current of dry purified air at 300°:

$$MnO_2 + 2NaOH + O = Na_2MnO_4 + H_2O \text{ (the inverse reaction also occurs).}$$

With twenty retorts in twenty-four hours 100 cu. metres of pure oxygen are produced.

The production of oxygen by electrolysis of copper sulphate has been proposed. By this means electrolytic copper, sulphur trioxide, and oxygen would be obtained, but there would always be danger of obtaining hydrogen mixed with the oxygen.

Oxygen is also obtained by the action of water on sodium peroxide, slowly in the cold, but rapidly on warming: $Na_2O_2 + H_2O = 2NaOH + O$. This method is used on the large scale for the bleaching of woollen and silken fabrics, but it is necessary to bear in mind that the alkaline action of sodium hydroxide is injurious to wool and silk; the alkali must therefore be neutralised with an acid as it is formed.

By means of this reaction, then, which takes place in the cold, we are able to produce conditions favourable to the oxygenation of the air and absorption of CO_2 in confined spaces in cases of illness or where large numbers of people are assembled, as the sodium hydrate which is formed absorbs CO_2; Na_2O_2 may, therefore, also be used in diving-bells, submarines, etc.

Coehn in 1894 (Ger. Pat. 75,930) proposed to electrolyse water, using a depolariser at the negative pole to avoid the evolution of hydrogen and collecting the oxygen at the positive pole; in order to utilise the half of the electrical energy which disappears at the negative pole through the action of the polariser, lead-accumulator plates are used for this purpose and become charged with electric energy. This method has not yet been actually used.

Among the various electrolytic methods, the best results have been obtained by the electrolysis of alkaline water by Garuti's system (*see* Hydrogen) or by that of Schuckert & Co. in Hanau, who since 1897 have used alkaline solutions with a non-porous diaphragm of vulcanite (*see* Hydrogen) producing oxygen at 0·48*d.* to 1·9*d.* per cubic metre as against 2*s.* per cubic metre by the chemical methods.

G. Kassner proposed in 1890 and perfected in 1900 his calcium plumbate method, which became of practical importance. Whilst oxygen prepared by other methods contained formerly only 75–80 per cent. of pure oxygen, by his process oxygen of 95–98 per cent. is obtained.

Kassner has further improved (1913) this process and now heats at 450° a mixture of sodium metaplumbate and sodium manganate ($Na_2PbO_3 + Na_2MnO_4 = MnO_2 + Na_4PbO_4 + O$)—termed *plumboxan*—and treats it with a current of steam, which causes immediate gradual evolution of oxygen. The spent hot mass is afterwards treated with a current of pure air, which regenerates the plumboxan. After removal of the nitrogen of the air by evacuation, the action of the steam (free from air) is repeated. These operations are thus carried out alternately. One kilo of plumboxan yields 1 litre of oxygen every five minutes at 400°, or double this quantity at 450°. The process appears to depend not on a reversible reaction, but on a catalytic action of the water; the regeneration of the plumboxan represents a different process from the liberation of the oxygen.

The electrolysis of bicarbonates may have a certain practical importance for the simultaneous preparation of oxygen, caustic soda, and hydrogen.

$$NaHCO_3 + H_2O = \underbrace{H_2 + NaOH}_{\text{negative pole}} + \underbrace{CO_2 + O}_{\text{positive pole}}$$

This method has been practically studied since 1901, but is not known to have achieved industrial success.

We may record on account of their curiosity the attempts made by Mazza to prepare oxygen by centrifuging air. The experiments were started at Turin in 1901 in a cylindrical sieve with a velocity of 1000 revolutions per minute (the process had already been patented by Claude of Paris). The results were absolutely negative and could not have been otherwise. The method has not taken into account the substantial difference between a liquid (such as milk) and a gas which has a very large molecular velocity (hydrogen about 2000 metres per second) and which would be influenced with difficulty by the ordinary methods at our disposal; to this must be added that the molecular velocity of oxygen differs but slightly from that of nitrogen. In 1906 Mazza believed that he had perfected his method, and took out new patents (*e.g.*, Austrian Pat. No. 55,308) based on the compression of air, which is then allowed to escape into curved tubes; the result is a kind of centrifugation leading to the separation of the components of the air.

The methods which are now contending for the ascendancy in the production of large quantities of oxygen at a cheap rate on a commercial scale are: Brin's method with barium oxide; the electrolytic method, by which very pure oxygen can be obtained (in practice as much as 3 per cent. of hydrogen may be present without any danger), the most used process of this character being that of Garuti, which we have described in the chapter on Hydrogen (in this case oxygen is also obtained, together with double the volume of hydrogen); finally the method by means of liquefaction of air, of which we shall give further details later (Liquid Air).

ANALYSIS OF OXYGEN. Ordinarily qualitative tests are made for impurities (CO_2, H_2S, Cl, etc.) by passing the gas through suitable reagents. The quantitative examination is usually confined to a determination of the quantity of oxygen absorbed by an alkaline solution of pyrogallol in the Orsat apparatus described later in the chapter on Carbon Dioxide.

ACTIVE OXYGEN

Until a few years ago this was supposed to be identical with ozone, but Baumann, Hoppe-Seyler, and Traube have all repeatedly shown that active oxygen has certain more energetic oxidising properties than ozone, since it oxidises CO to CO_2, even in the cold.

Active oxygen is formed particularly by contact of air with water under certain conditions, also by contact of O with hydrogenised palladium and by phosphorus in contact with air and water, in which case hydrogen peroxide and ozone are also formed.

It is supposed that active oxygen is oxygen in the atomic state, and that this accounts for its great chemical activity. A substance capable of activating oxygen—other than hydrogenised palladium, phosphorus, etc.—is turpentine, which exerts this power strongly in the cold, and still more intensely at 100°.

Engler and his pupils have devoted themselves more especially, during the last few years (1898–1901), to the study of active oxygen, and have arrived at the hypothesis that it is not composed of atoms of free oxygen, but that it forms, with the activating compounds, a species of peroxides of oxygen, which very easily cede one atom of very active oxygen in various chemical reactions.

The question is not yet completely settled.

OZONE : O_3

Van Marum noticed, in 1785, the special odour which is developed when electric discharges take place in oxygen or air, and how these gases have then the capacity of increasing the brilliancy of mercury. It was not until 1840 that Schönbein discovered the cause of this phenomenon, and named the substance which was formed and had this odour, and which he succeeded in preparing by various methods, *ozone*. He prepared it, mixed with oxygen, by electrolysis of water, and by the slow combustion of phosphorus.

Ozone and hydrogen peroxide are present in small quantities in atmospheric air. De Thierry determined the ozone at various altitudes; at 1050 metres he found 3·5 mgrms. per cubic metre of air, and at 3020 metres he found 9·4 mgrms. per cubic metre (four times more than in Paris). Ozone is formed in the neighbourhood of waterfalls, and in general is abundant where much water is evaporated spontaneously. During thunderstorms appreciable quantities of ozone are formed.

According to Arnold, fresh unboiled milk turns guaiacum tincture blue and, therefore, contains ozone (?). It is assumed by many that the oxygen expired by plants contains ozone, but this is not the case.

FORMATION OF OZONE. Ozone is formed on heating peroxides, *e. g.*, barium peroxide, BaO_2, or potassium permanganate, with strong sulphuric acid, or on heating peroxides in a current of oxygen to the temperature at which they decompose:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O + O \text{ rich in ozone.}$$

Ozone is formed during the electrolysis of water together with the oxygen at the positive pole. It is formed by slow oxidation in a large bottle containing moistened phosphorus, partly immersed in water, and still more easily if a few drops of bichromate are added. It is also formed on burning hydrocarbons or by passing electric discharges through oxygen or air. It is formed during the electrolysis of sulphuric acid by means of a continuous current, and after the removal of various gases as much as 12 per cent. of ozone may be present.

Ozone is also formed when free fluorine acts on water at 0° (Moissan, 1899).

Generally speaking, one is unable to transform more than 9 per cent. of the oxygen present into ozone (whether it is pure or present in the diluted form as air).

However, F. Fischer and K. Massenez (1907) obtained oxygen containing 23 to 28 per cent. of ozone by electrolysing sulphuric acid of density below 1·223 (best 1·07) by a current of 80 amps. per sq. cm., cooling the platinum electrodes continuously. By working at a tension of 7·8 volts they obtained a yield of 7·2 grms. of ozone per kw.-hour.

Nernst showed in 1903 that free atoms of oxygen condense to ozone only when their concentration is ten to twenty times greater than in ordinary oxygen. The equilibrium conditions for the system ozone-oxygen at high temperatures can be calculated to be 0·3 per cent. of ozone at the absolute temperature of 1569°, 1 per cent. at 2321° absolute, and 10 per cent. of ozone at 4773° absolute; it can hence be deduced that ordinary oxygen should be transformed spontaneously into ozone when exposed to an elevated temperature and pressure. In order to separate the ozone rapidly in such a manner that it should not decompose, it was passed directly at this elevated temperature into liquid air, and the nitrogen oxides which had formed together with the ozone then separated as a flocculent solid, whilst the ozone remained in solution, and on filtering the liquid air to remove the nitrogen oxides and then evaporating it, the liquid ozone remained; it was of an intense blue colour and evaporated at $-119°$. Ozone is formed very easily by passing the electric arc through liquid air or, better still, through liquid oxygen so as to avoid the formation of nitrogen oxides.

Ozone is also formed by impinging a jet of air on to a Nernst lamp (1909); also by the action of ultra-violet rays from an electric mercury lamp with a bulb of quartz, which does not absorb the ultra-violet rays as does glass.

PROPERTIES. Ozone is a relatively stable gas which decomposes slowly at the ordinary temperature and rapidly at 400°; therefore on passing ozone through a red-hot tube it is transformed into oxygen, and no longer shows the characteristic reactions of ozone (*see below*); during this transformation its volume is increased, as two molecules of ozone produce three of oxygen.

It is slightly soluble in water; it dissolves and combines with the ethereal oils, especially with oil of turpentine and cinnamon oil, and with aqueous quinine solutions; it is somewhat soluble in paraldehyde.

Ozone is an endothermic substance and requires for its formation 151·5 Kj. (36,208 cals.), hence its lack of stability and greater oxidising power when compared with oxygen.

Being an energetic oxidising agent, it decolorises solutions of litmus and of indigo; it transforms phosphorus, sulphur, and arsenic into the corresponding acids, converts sulphides into sulphates, nitrogen into the oxide, N_2O_3, and also into ammonium nitrite and nitrate in presence of water. Even minimal traces of manganese salts in aqueous solution are quantitatively precipitated by ozone as MnO_2. It attacks almost all organic compounds, and rapidly corrodes rubber tubing and stoppers of cork or vulcanised rubber; only the albuminoids and the saturated hydrocarbons are attacked but slightly or not at all. With certain organic compounds it produces a species of phosphorescence. It oxidises methane quantitatively to formaldehyde. Inorganic substances (salts) it oxidises with only one atom of active oxygen ($O_3 = O_2 + O$), whilst with organic compounds (and also with $SnCl_2$) the three atoms of oxygen react ($O_3 = 3O$). With solid caustic alkalis or with liquid ammonia it gives an orange coloration. Ag and Pb are converted into black peroxides and iodine into I_4O_9.

Silver, however, forms the peroxide only in places where it is already covered with a trace of invisible oxide (*e. g.*, by heating the silver to 200°).

Harries found that unsaturated organic compounds form with ozone well-defined compounds (ozonides), and Molinari and Soncini showed that oils and fatty acids containing unsaturated compounds with a double linking between carbon and carbon absorb ozone quantitatively, with formation of characteristic ozonides. In 1906 Molinari showed further that unsaturated organic compounds with a triple bond between carbon and carbon do not absorb ozone, and in this way the two classes of unsaturated compounds may be distinguished.

Ozone has a strong bactericidal action (*see* Water).

LIQUID OZONE. Until a few years ago ozone had never been isolated and was known only by its odour and by certain chemical reactions, but always in admixture with much air or oxygen. In 1898 Troost, and afterwards Ladenburg, liquefied the mixture of air and ozone by cooling with liquid air; on allowing the oxygen to evaporate they then obtained an opaque blue liquid consisting of pure liquid ozone, boiling at $-119°$, which easily exploded.

CHARACTERISTIC REACTIONS OF OZONE. Ozone was detected in the air by Schönbein by the blue coloration with starch paste and potassium iodide, due to the liberation of iodine which colours the starch. It must, however, be noted that this reaction is also shown by the higher oxides of nitrogen and by hydrogen peroxide, all of which always occur in the atmosphere. This reaction of ozone does not occur after the air is passed through a hot tube (Andrews), hydrogen peroxide behaving similarly.

In 1868 Houzeau showed that during the blue reaction of ozone and of hydrogen peroxide with starch and potassium iodide an alkaline reaction is also produced, whilst this is not the case with the reaction produced by oxides of nitrogen: $2KI + O_3 + H_2O = 2I + O_2 + 2KOH$ and also $2KI + H_2O_2 = 2I + 2KOH$. There still remains the doubt whether the Schönbein reaction is due to ozone or to hydrogen peroxide.

Numerous attempts were made to discover a characteristic reaction of ozone which would distinguish it from the oxides of nitrogen, the halogens, and more especially from hydrogen peroxide. Potassium iodide, metallic silver and lead, guaiacol tincture (with a trace of iron sulphate, which becomes blue with ozone), manganese sulphate, lead acetate, thallium hydroxide, etc., were for long all considered in turn to be capable of characterising ozone, but recent work of Anord and of Mentzel (1902) decides unfavourably against the use of any of these reagents, and the only one which remains is benzidine (p-p′-diaminodiphenyl), which becomes brown with ozone only, whilst the oxides of nitrogen and bromine turn it blue; with chlorine it passes through blue to reddish brown and with hydrogen peroxide it gives no reaction. If, however, a drop of a 10 per cent. copper sulphate solution is added to the benzidine solution it gives a blue precipitate with H_2O_2, whilst with ozone it gives a reddish-yellow precipitate.

According to F. Fischer and Marx (1906) it is better to use paper impregnated with a methyl alcoholic solution of tetramethyl-p-p′-diaminodiphenylmethane (called *tetrabase*) to which a drop of acetic acid has been added; when moistened, this gives with ozone a pale violet coloration, whilst with nitrous oxide the coloration obtained is yellow to dirty brown; with hydrogen peroxide it does not react even in presence of copper sulphate, and chlorine and bromine give a deep blue coloration.

H. Kayser and Master (1908) distinguish between the components of a mixture of ozone, nitrogen peroxide, and hydrogen peroxide in the following manner: The gas is passed through a dilute permanganate solution, which absorbs the NO_2 and H_2O_2, but not the ozone, which is detected with KI. Nitrogen peroxide and hydrogen peroxide decolorise the dilute permanganate solution. Another portion of the mixture is passed over a layer of manganese dioxide which decomposes both ozone and hydrogen peroxide, whilst nitrogen peroxide remains unaltered and is able to decolorise a dilute permanganate solution, or to produce nitrite (detected with anilinesulphonic acid and α-naphthylamine) if passed into a solution of pure sodium hydroxide free from nitrites (even when mixed with ozone and H_2O_2). Finally, hydrogen peroxide is detected in the presence of the other two gases by passing them through a brown solution of potassium ferrocyanide and ferric chloride, in which hydrogen peroxide alone produces a characteristic green or blue coloration of Prussian blue.

With solid caustic potash ozone gives a deep brown compound which is decomposed, with evolution of gas, by water; further, concentrated KOH solutions give a yellowish-brown coloration at a temperature below zero. Rubidium and cæsium behave similarly, whilst caustic soda is coloured only faint yellow (Baeyer and Villiger, 1902). These reactions are due to the formation of a mixture of various higher oxides, which do not, however, yield hydrogen peroxide when treated with water (W. Traube, 1912).

Metals and organic substances which have been acted on by ozone become radio-active and affect the photographic plate.

CONSTITUTION OF OZONE. After many experiments, Williamson and Baumert, independently of one another, pronounced ozone to be an oxide of hydrogen peroxide, H_2O_3. Marignac, Delarive, and Cahours maintained, without being able to prove it, that ozone must be a more condensed oxygen molecule (allotropic oxygen). This was, however, shown with certainty by Andrews and Tait.

The molecular weight, corresponding with O_3, was determined with the diffusiometer by Soret in 1886 and confirmed by M. Otto in 1897, but doubt was thrown on these determinations by Städel in 1899. The recent work of Ladenburg in 1901 and 1902 has, however, definitely confirmed the fact that the molecule of ozone consists of an aggregate of three atoms of oxygen. This may also be demonstrated by a very simple experiment; thus Soret passed the silent electric discharge for some time through a given volume of oxygen, and noted the diminution of volume caused by the formation of ozone. He then placed half the remaining volume of ozone and oxygen in contact with oil of turpentine and measured the diminution of volume (due to absorption of ozone): he heated the other half and noted the increase of volume due to conversion of ozone into oxygen. He was thus able to determine the relation between the weight of ozone and that of the same volume of oxygen, and found that the ozone weighed one and a half times as much as oxygen, and that two volumes of ozone gave three volumes of oxygen.

On the other hand, if mercury is placed in contact with a given volume of ozonised oxygen, the mercury is oxidised at the expense of an atom of oxygen from the ozone, and oxygen remains, but without alteration of volume; 2 vols. $O_3 + 2Hg = 2$ vols. $O_2 + 2HgO$. Ozone is thus an allotropic form of oxygen, and from these two examples we may infer that the ultimate particles of matter are not molecules, but atoms or perhaps still smaller units.

In general if an element is known in various forms, with different properties, containing varying amounts of energy, these forms are called *allotropic*. The difference between oxygen and ozone is due to the larger amount of energy contained in the latter.

APPLICATIONS OF OZONE. The most important of all is the sterilisation of water to render it potable. This most important subject will be discussed in detail later in the chapter on Water.

Ozone is used in medicine by being inhaled, diluted with much air and free from nitrogen oxides, by those suffering from pulmonary infection. In France a therapeutic institute for the use of ozone was started in 1909.

Much has been written concerning the value of ozone as a deodorant and disinfectant of the air in closed, infected places (theatres, churches, schools, etc.)—the air is moved through fans which produce ozone—but its bactericidal action in dry air seems now almost entirely disproved. Indeed Konrich (1912) and, in some degree, Czapleroski (1913) disputed the advantages of ozone for ventilating compartments, since the dry bacteria found in the air are not killed; they therefore advised the purification of air by frequent renewal.

The deodorising effect of ozone is almost universally admitted. According to Czapleroski (1913) this gas hinders the formation of moulds and transforms ammonia into nitrous acid; it is uncertain if H_2S is oxidised by it, but carbon monoxide remains unchanged, although indole and scatole (causing the stench of intestinal gas) are decomposed; butyric and valeric acids are unaltered: iodoform is decomposed and the odour of tobacco smoke partially dissipated. The enclosed air of underground compartments and of closed spaces generally is greatly deodorised and improved by circulating it through an ozonising fan or, better, by the injection of ozonised air. If, however, the latter contains more than 0·1 mgrm. of ozone per cu. metre, it is not well suited for respiration, while for the disinfection of articles or the preservation of foodstuffs 0·3 mgrm. per cu. metre may be present.

Frölich proposes the use of ozone to combat phylloxera, but it does not appear to be of practical use in this connection. Trillat employs it as an oxidising agent in the perfume industry, and transforms 25 kilos of isoeugenol into vanillin in one operation. The Société Anglo-Française of Courbevoie prepares notable quantities of piperonal (heliotropin) and vanillin in this way. The latter cost £360 per kilo in 1876, £28 per kilo in 1890, and now less than £4 per kilo. In 1904 the new Ozone Vanillin Company was formed at Niagara Falls with a capital of £80,000.

The employment of ozone for bleaching textile fibres is perhaps premature, as it cannot compete in price with chlorine and is not suitable for bleaching silk or wool, as its bleaching powers are not large.

In the Bouillaut sugar refinery at Noyon, France, the sugar syrup is treated with ozone to remove organic impurities; in this way crystallisation is facilitated and less molasses obtained; the action of the ozone is followed by treatment with sulphuric acid, the latter being afterwards removed with barium oxide and the liquor passed on to the filter-presses.

Engledew, in England, declared that he had perfectly purified foul beer casks, which could not be cleaned in any other way, by the use of ozone, and maintained that a large brewery would soon save the cost of a plant for the production of ozone. According to Moufang (1912) such casks are cleansed more readily with ozonised water than with ozonised air.

Ozone has also given good results for ageing highly alcoholic wines and liqueurs.

It does not appear to have been successful for the bleaching of flour, as this acquires an unpleasant taste and odour.

It has been proposed and tried, with uncertain and often negative results, for the manufacture of vinegar (from eight parts of water and two of alcohol), for the purification of alcohol from fusel oil, for bleaching fats, oils, sugar syrups (molasses), mineral oils, etc. Many optimistic expectations on the application of ozone have proved delusive, but the experiments should certainly be tried again under other and more rigorous conditions.

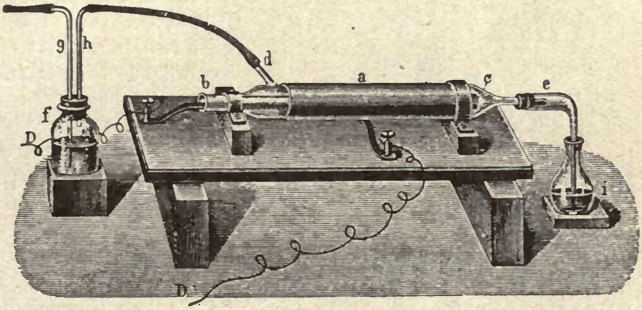


Fig. 70.

By decomposing the ozonides of oleic acid and other oils by the method of Molinari and Soncini (1906) nonylic and azelaic acids can be prepared at a price of about 6*s.* 6*d.* to 8*s.* per kilo, whilst formerly those two acids cost about £20.

The last word on the applications of ozone has not yet been said, and the future will perhaps bring surprises. Ozone at its present price cannot be used except in industrial processes yielding products of great value, such as vanillin, etc., or for the sterilisation of water, which is attained with a relatively very small quantity of ozone.

INDUSTRIAL PREPARATION OF OZONE. Until a few years ago ozone was not of much practical importance and was prepared in minimal quantities in the laboratory by means of the silent electric discharge at high tension, in an atmosphere of oxygen or air.

Use was made of an apparatus devised by Siemens as long ago as 1857 and consisting of two concentric glass tubes (Fig. 70), of which the inner was filled with tin in connection with one pole of a Ruhmkorff coil and the outer covered with tinfoil connected with the other pole of the induction coil; a current of air or oxygen was passed between the two tubes, whilst the silent discharge passed across, producing numerous blue sparks.

The quantities of ozone obtained were very small, and appreciable quantities were only obtained with an improvement devised by Fröhlich in 1891. He constructed ozonisers with an internal tube of aluminium or tin and an external tube of celluloid, mica, or paper covered with tinfoil, the internal tube being cooled by a continuous current of water. He succeeded in preparing 4·5 grms. of ozone, diluted with much air, by means of a battery of ten such ozonisers with an expenditure of one h.p.-hour of energy.

Berthelot advantageously replaced the metallic coverings by dilute solutions of sulphuric acid or simply by water, using the very simple glass apparatus shown in Fig. 71. The tube *g* closes the mouth of a wider tube, which has an inlet tube, *o*, conducting the air or oxygen to the apparatus and between the walls of the two main tubes, and an outlet tube, *s*, through which the ozonised gas escapes. The tube *g* is full of water into which dips an aluminium wire, forming one of the electrodes of a high-tension current (10,000 to 12,000 volts); the whole apparatus is suspended in a larger vessel, *w*, also filled with water, into which the other aluminium electrode, *d*, dips. In the dark the blue discharge between the two tubes is easily seen. These ozonisers are arranged in batteries of four, six, or ten such tubes, and the ozonised air is collected in a single tube of glass or metal leading to the reaction chamber, care being taken that all the joints are of glass or are sealed with mercury.

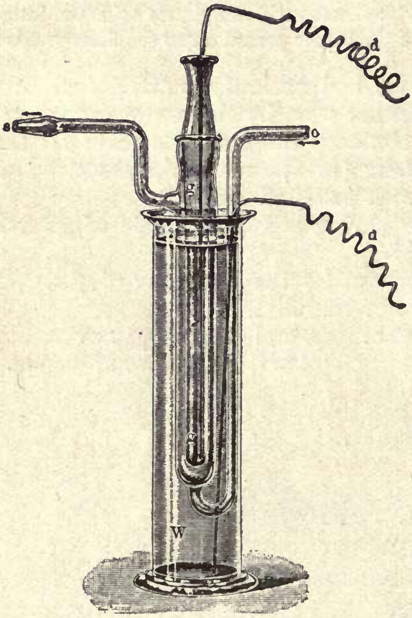


FIG. 71.

For the production of ozone high-tension currents at 6000 or 10,000 volts and certainly not less than 4000 volts are required; some forms of apparatus require 50,000 volts. Rotary commutators are generally found serviceable. Care must always be taken that very dry air or oxygen is employed, though when working at a low temperature (0°) a little moisture is permissible; in general dry air yields six times as much ozone as moist air. The yield of ozone diminishes with rise of temperature but increases when the pressure is raised. In all cases a part of the oxygen only is converted into ozone and under no circumstances more than 9 per cent. The quantity of ozone formed is always in the same proportion to the oxygen present whether pure oxygen or air is used; in the latter case the ozone is obtained in a more dilute state, but also more cheaply, as the air costs nothing.

In 1896 Andreoli, in London (Ger. Pat. 96,058), patented a very ingenious ozoniser which paved the way for the industrial preparation of ozone.

Another more complicated but well-designed apparatus is that of Otto (Ger. Pats. 96,400 and 129,688) in which the danger of short circuits is avoided and a silent discharge of numerous blue sparks is obtained, without any arcing. At first very dilute currents of ozonised air were obtained, but the apparatus was ultimately applied in various industries and for the production of potable water (at Nice).

Many other forms of apparatus were then patented, but few only found application. Among these we must also mention those of Otto, Verley, and Marmier-Abrahm, and the more important ozonisers, constructed for large output, of the firm of Siemens and Halske, Berlin. These are formed of iron boxes (Fig. 72) weighing 40 kilos in all, and containing eight ozonising tubes, fixed inside the box between two planks and hermetically sealed.

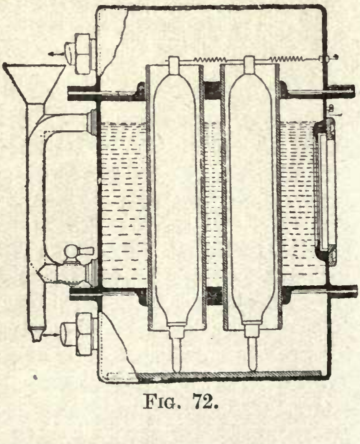


FIG. 72.

In the middle compartment cold water circulates round the eight tubes; perfectly dry air is passed into the lower compartment, enters the space between the two tubes of each ozoniser, and when ozonised enters the top compartment.

The ozonising tubes consist of an external tube of glass or porcelain, cooled by the water, and a concentric internal tube of metal, varnished with a substance resistant to ozone or simply formed of aluminium. The space between the two tubes, through which the air passes, is a few millimetres wide. The internal tubes communicate with one pole of the high-tension current, by means of perfectly insulated wires which are enclosed in the supporting columns of the apparatus and thus avoid all danger to those who work or touch the apparatus; their safety is further provided for by the fact that the other pole is connected to earth by means of the water which circulates continuously through the apparatus. The box containing the eight ozonising tubes has a glass front so that one can at any moment see the blue colour of the sparks of the silent discharge and so assure oneself that the apparatus is in order. There are also devices which ensure automatic interruption of the current in case of breakage.

With the Siemens-Halske ozonisers more than 60 grms. of ozone per h.p.-hour can be obtained. The air to be ozonised is previously dried, either by condensing the moisture by passage through an ice-machine, or, better still, by passing it through strongly hygroscopic substances, such as lime, sulphuric acid, fused calcium chloride, etc. Fischer (Ger. Pat. 187,493 of 1907) obtained concentrated (30 per cent.) ozone by electrolysis of cooled dilute sulphuric acid.

ANALYSIS OF OZONE. Now that the industrial importance of ozone has become so great, a knowledge of the amount of ozone contained in a given volume of air or produced by an ozoniser is often required. A given volume of the ozonised air is passed through a neutral solution of potassium iodide; this is then acidified and the liberated iodine titrated with a solution of sodium thiosulphate of known strength. An alkaline potassium iodide solution may also be used; in this case an iodate is formed, so that, after acidification of the liquid, the free iodine may be titrated in the usual way (G. Lechour, 1911, and E. Czakò, 1912). Ladenburg, Quasig, Treadwell, and Anneler, on the other hand, first weigh a bulb full of oxygen, and then weigh it when full of the ozonised gas. The difference of weight multiplied by 3 gives the weight of ozone.

A convenient and exact method for large quantities has been studied by Fenaroli (Soc. chim. di Milano, 1906) and is based on the property of the unsaturated fats and fatty acids (oleins) of absorbing ozone quantitatively, as shown by Molinari and Soncini. All that is therefore required is to pass a known quantity of the ozonised air through a weighed quantity of olein and to determine the increase of weight of the latter, which gives the amount of ozone. Ruata showed in 1910 that this method is more exact than that with potassium iodide. F. Krüger and M. Moeller (1912) maintain that the optical determination (based on the great absorption occurring in the zone of wave-lengths, 200–300 $\mu\mu$) is more sensitive than the chemical determination.

ANTIOZONE. Schönbein believed in the existence of electropositive ozone, in addition to the electronegative ozone already known, and attempted to show that it had certain characteristic reactions. Several chemists showed, however, that it did not exist, and that hydrogen peroxide vapour had been mistaken for it. To-day the conception of antiozone has again been revived and it appears to be nothing but atomic or ionic oxygen liberated from ozone.

SULPHUR: S, 32.07

Sulphur was already known to the ancients, and was employed as a medicine and for fumigation, as was recorded by Homer, 900 years before Christ. More recently it was used for bleaching textile fibres.

In the Middle Ages it was considered by Gebir, about the year 800, to be one of the two components of metals, sulphur and mercury, and it was then believed to be possible to pass from one metal to another by increasing or diminishing one or other of these components; with more mercury one expected to obtain the more brilliant metals, silver and gold, and with more sulphur the baser metals such as copper, iron, etc.

It was known to the alchemists that sulphur dissolved in aqueous alkaline solutions, and that from these it was liberated by acids as milk of sulphur. It was also known that it dissolved in *aqua regia*, but it was not known that in this way the sulphur was transformed. It was known that it dissolved in some oils, and balsams with a sulphur base were thus prepared.

Sulphur kilns were first recorded by Basil Valentine (1456). At the period of the phlogiston theory sulphur was considered to be a combination of phlogiston with an acid.

Lavoisier recognised it to be a simple substance; all the same, Davy, in 1809, held it to be a species of resin, but after that time sulphur was considered as an element.

In nature it is found in various forms:

(1) In the native state, that is, ready formed, crystalline, or mixed with gypsum and earthy matter; the most abundant natural source (over 80 per cent. of all native sulphur) is in this last condition. Native sulphur occurs also in and about active and extinct volcanoes.

(2) It is found as metallic sulphides, such as iron and copper pyrites, zinc blende (ZnS), galena (PbS), etc.

(3) As hydrogen sulphide (H_2S) in sulphurous springs, sometimes accompanied by carbon oxysulphide.

(4) As sulphur dioxide (SO_2) in volcanic fumes.

(5) As sulphates in various mineral deposits.

(6) In organic substances, especially nitrogenous substances, such as albuminoids, hair, horn, etc. It is also found free in certain bacteria (Beggiatoa) and in the cells of some algæ (*e. g.*, Oscillaria and Ulothrix).

PHYSICAL PROPERTIES OF SULPHUR. Solid sulphur has a bright yellow colour, which almost disappears at − 50°, and becomes more intense at 100°. It is insoluble in water, slightly volatile with steam, and very slightly soluble in alcohol, ether, ethereal oils, and fats. It is very soluble in carbon disulphide (39 per cent. in the cold and 74 to 180 per cent. when heated), in sulphur chloride, and in hot aniline (80 per cent.); it is also soluble in petroleum ether (*see* Vol. II.). Sulphur crystallises from carbon disulphide in large rhombic crystals. It is easily electrified by friction.

Its specific gravity is 1·92 (amorphous) or 2·06 (rhombic). It melts at 114·5° (rhombic) or 119° (monoclinic), yielding a yellow mobile liquid, which acquires a deep orange colour at 160°; at 220° it becomes viscid, reddish, and adhesive, and between 240° and 260° is still more consistent and viscous, and of a red-brown colour; beyond 340° it again becomes a little more liquid, but remains dark, and at 445° it commences to boil, giving red-brown vapours.

The theoretical temperature of combustion of sulphur with the calculated quantity of air is 1616° at constant pressure and 2000° at constant volume. With the excess of air practically used in pyrites burners, the temperature reached should be 900° according to theory; the temperature actually reached is about 550°, and it should not be below 500°, since with gases containing 10 per cent. of SO_2 the temperature of ignition is 465°, so that boiling sulphur then distils without burning. In presence of a large excess of air the temperature of ignition falls to 250°, as in combustion furnaces for the extraction of sulphur from ores; at this temperature the fused sulphur is somewhat viscous, but if less air were used the temperature of ignition would rise to 300°–340° and the sulphur then become mobile.

Sulphur is known in three conditions or allotropic forms: The most stable condition is rhombic sulphur (α-sulphur), in octahedra, which are generally obtained when it is crystallised at ordinary temperatures and from various solvents, such as carbon disulphide.

Another form is prismatic sulphur (β-sulphur) of the monoclinic system; this is obtained from hot solvents (alcohol and benzene) and is stable above 95°. At ordinary temperatures this form is slowly and spontaneously converted into the rhombic form, with evolution of heat (72·6 cals. per 32 grms. of sulphur).

A third form of sulphur (γ-) is amorphous and plastic, and is obtained by pouring boiling fused sulphur into water; it is insoluble in carbon disulphide, and is darkened in colour, even to blackness, by minimal traces of organic compounds (fats, paraffin, etc.).

A further variety of amorphous sulphur is that which is obtained from solutions of hyposulphites or polysulphides with acids (precipitated sulphur, magister of sulphur[1]). It has a whitish appearance and is soluble in carbon disulphide.

When sulphur is heated with soda, it yields black amorphous sulphur, which, when thrown into fused borax or calcium chloride, acquires an intense blue colour. A blue colour is also formed on heating sodium thiocyanate (NaCNS) to 430° (Paterno and Mazzucchelli, 1907).

Other varieties of sulphur have been prepared; thus, for instance, on passing hydrogen sulphide into a solution of SO_2, sulphur soluble in water (colloidal sulphur or δ-sulphur) is prepared, and is obtained even more readily (according to Sarazon, 1910) by passing SO_2 into a saturated solution of H_2S in glycerine (Ger. Pat. 216,825).

The amounts of heat required to reduce the different varieties of sulphur to the molten state (referred to 100°) are 14·9 cals. per gram for rhombic sulphur and 11·5 cals. for the monoclinic form. Closely similar values are obtained for the transformation into γ-sulphur. To transform the latter into μ-sulphur in the liquid state, 13 cals. are required. The specific heat of liquid λ-sulphur is $0{\cdot}21 + 0{\cdot}00016\,t$.

According to the vapour density at low temperatures the molecule of sulphur is S_8; as the temperature is raised dissociation commences, and at 850°–900° only S_2 molecules are left. The molecule S_6 appears not to exist, and the variety of sulphur insoluble in carbon disulphide ($S\mu$) perhaps corresponds with the molecule S_8.[2]

The colour of sulphur vapour is orange slightly above the boiling-point and redder at 500°, becoming rapidly lighter at higher temperatures. On passing a current of air over sulphur at a temperature slightly below 200° a marked odour of camphor is produced (perhaps inherent to sulphur vapour); above 200° the sulphur oxidises slightly, emitting a phosphorescent light, and at 250° the air current contains ozone, but is not ionised (difference from phosphorus: Bloch, 1909). The valency of sulphur varies in its different compounds; it is divalent in hydrogen sulphide, SH_2, tetravalent in sulphur dioxide, SO_2, and hexavalent in sulphur trioxide, SO_3.

We have seen that at low temperatures sulphur always exists in the rhombic form, that is, in octahedra, like the natural sulphur found in the mines. If such sulphur is heated slowly in a suitable dilatometer its volume is observed to increase uniformly with the rise of temperature until it attains the temperature of 95·4°, when there is an abrupt and notable increase of volume and the sulphur, which was light yellow, acquires a much more intense, almost orange, colour; the sulphur has been transformed at this temperature into monoclinic sulphur. The two forms of sulphur have different melting-points;

---

[1] Precipitated sulphur (magister of sulphur) is prepared as follows: One part of quicklime is made to a paste with 5 parts of water, and 2 parts of flowers of sulphur are added; a further 24 parts of water are then added and the whole boiled in an iron vessel until all the sulphur is dissolved, the water being replaced as it evaporates. The liquid is decanted after settling and the residue treated with several successive small quantities of water, boiled for half an hour and filtered. The liquids thus obtained, containing calcium polysulphides, are brought to a specific gravity of about 8° Bé., and hydrochloric acid, diluted to 10° Bé. and free from arsenic, iron, and sulphuric acid, is then added little by little, with vigorous stirring, either under a hood or in the open, until only a very slight alkaline reaction remains (due to unaltered calcium sulphide). The very fine precipitated sulphur is at once collected on a cloth filter and washed until the washings no longer become turbid with silver nitrate solution. It is then dried at 30°. It is well to treat with the acid in a closed apparatus with a delivery tube to carry off the hydrogen sulphide, which is abundantly formed (and is very poisonous), up a chimney. If the operator should inhale the H_2S he loses his senses; the best method of treatment is to drench him quickly with much cold water, otherwise he remains under the influence of the poison. The calcium polysulphide is formed according to the following reaction: $3CaO + 11S = CaSO_3 + 2CaS_5$. The calcium pentasulphide reacts with the acid as follows: $CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$. Precipitated sulphur is sometimes adulterated with gypsum or other mineral substances, but these can be detected by incineration. Pure sulphur leaves no residue (less than 0·5 per cent.).

[2] γ-sulphur is partially soluble in carbon disulphide and is a mixture of the λ- and μ-varieties.

when rhombic sulphur is heated rapidly, so that it has not time to be transformed into prismatic sulphur, the melting-point is found to be 114·5°, whilst when prismatic sulphur is heated or rhombic sulphur heated slowly, the melting-point is found to be 119°. Rhombic sulphur has a specific gravity of 2·06, whilst that of prismatic sulphur is 1·92. At temperatures below 95·4° monoclinic sulphur slowly becomes rhombic. The temperature 95·4°, at which the two forms are able to co-exist, is called the *point of transformation.*

The two forms of sulphur have the same vapour pressure at the transformation point. A substance which can be modified, like sulphur, in two senses at the point of transformation is called *enantiotropic ;* the melting-point of that modification which melts first is always higher than the transformation point of the two substances, for if it were lower we should have a *monotropic* substance which could change only in a single sense at the point of transformation. In point of fact, in some cases the less stable modification melts below the transformation point (*e.g.*, iodine chloride, ICl, in which the less stable modification melts at 14°, and the more stable at 27°).

If a crucible of molten sulphur is allowed to cool slowly, and then, when it is covered with a crust of solidified sulphur, this is broken and the liquid sulphur poured off, needle-shaped monoclinic crystals are found in the crucible; if these are allowed to cool they become lighter in colour, and though they preserve their external form they are then found to be formed of a large number of small octahedra; thus internal transformation has taken place and the needle-shaped crystals are called *pseodomorphs.*

If we consider the transformations of sulphur in connection with the phase rule we are able to compare its behaviour with that of ice and water. These can co-exist in complete equilibrium only at the temperature 0·0075°, because only at this temperature can the sole component (H_2O) be present as the three phases, ice, water, and water vapour. The point at which the three phases can co-exist is called the triple point, or in general, for more phases than one, the multiple point. On pp. 120–122 we have demonstrated that for a system of n components equilibrium is complete only when $n + 2$ phases are present; for each phase the pressure, temperature, and composition are then fixed.

If in such a system the pressure remains constant and the temperature varies, or *vice versa,* one of the phases disappears and complete equilibrium ceases. If of such a system two phases remain ($n + 1$, *e. g.*, liquid water and vapour) the equilibrium is incomplete, but determined, and we speak of a *monovariant* system (*see* p. 121) because equilibrium between the two phases can exist at various temperatures provided that with each of these there corresponds a determinate pressure, or *vice versa ;* if, on the other hand, the temperature remains constant whilst the pressure is continuously varied, or *vice versa,* then one of the phases will disappear and this determined equilibrium will also cease, and only vapour or only liquid water will remain. By altering the pressure in the complete equilibrium of three phases, water, ice, and vapour, we are able to displace, by a very small amount, the point of transformation (melting-point of ice). This theoretical deduction has been experimentally confirmed, and we know now that for each atmosphere of pressure the fusion point of ice is altered by 0·0079°, and that 136 atmospheres are required to displace it by one degree.

By means of the phase rule we can explain the transformations of sulphur into its various modifications. Below 95·4° we have two phases, namely, solid rhombic sulphur and sulphur vapour[1]; above that temperature we have, on the other hand, the phase of monoclinic sulphur and sulphur vapour, the pressure of which is variable up to 119° (melting-point of monoclinic sulphur). At the temperature of 95·4° we have the triple point, at which the three phases of sulphur can co-exist, namely, monoclinic sulphur, rhombic sulphur, and sulphur vapour; at this point equilibrium is complete, as we have three phases and only one component, S.

In this case also, as in that of ice, the point of transformation (triple point) varies with variation of the pressure, and by exactly 0·05° for each atmosphere. At 119° we have another triple point, that is, three phases can coexist in equilibrium : solid monoclinic sulphur, liquid sulphur, and sulphur vapour. Between 95·4° and 119° we have incomplete but determined equilibrium, that is, we have a monovariant system (one component with two phases—solid sulphur and sulphur vapour) and the equilibrium is determined,

---

[1] We must suppose that solids also have a vapour pressure, though this may be very small. In the case of ice it is easily measurable, but for other solid substances it is so small as to be unmeasurable by ordinary methods.

because for any given temperature between these limits there is also a fixed and definite pressure at which equilibrium is still able to exist, and *vice versa* on fixing the pressure the temperature is similarly determined.

On p. 121 we have studied the bivariant systems and explained the behaviour of non-saturated solutions of a salt, where we have two components, salt and water, with two phases, liquid solution and vapour. In this case, the composition of the solution being fixed, the temperature and the pressure must be fixed, that is, there is only a single concentration of the solution which at a given temperature possesses a definite vapour pressure. The equilibrium is in this case of two dimensions.

CHEMICAL PROPERTIES OF SULPHUR. When sulphur is heated in the air it burns with a pale bluish flame, giving sulphur dioxide: $S + O_2 = SO_2$. It also burns in pure oxygen, to form the same compound (without alteration of volume). If, however, compounds are present which generate active oxygen, or catalysers, such as platinum sponge, iron oxide, etc., sulphur trioxide (sulphuric anhydride) is formed directly with diminution of volume (*see* Catalytic Sulphuric Acid *below*): $S + 3$ vols. $O_2 = 2$ vols. SO_3. On burning, 1 kilo of sulphur evolves 2165 calories.

Sulphur combines directly with the greater number of metals and non-metals, and in varying quantities with the same element. Thus, *e. g.*, it forms trisulphides and pentasulphides of arsenic, antimony, etc.

A hot copper spiral burns directly in sulphur vapour.

Flowers of sulphur commonly show an acid reaction, owing to the formation of traces of sulphuric and sulphurous acids. The acid reaction may be removed by repeated washing with water.

Sulphur combines with hydrogen to form H_2S. Oxygen burns in sulphur vapour, and it is thus both a combustible and a supporter of combustion.

USES OF SULPHUR. The greater part serves for the preparation of pure H_2SO_4, of SO_2, and of salts related to these (sulphates, sulphites, thiosulphates). It serves also for the preparation of metallic sulphides, gunpowder, and carbon disulphide, for the vulcanisation of rubber and guttapercha, for bleaching silk and wool (*see* Vol. II), and for treating with sulphur dioxide wine and beer barrels, in order to remove from the wine the odour of hydrogen sulphide:

$$2H_2S + SO_2 = 2H_2O + S_3.$$

It is used in the wine-growing industry against a cryptogam which attacks the young bunches of grapes and shoots of the vine; this is a microscopic fungus, oidium (or *Uncinula Americana*), the reproductive and vegetative system of which simply adheres to the surface of the part attacked and does not penetrate, as does *Peronospora*. The latter develops in the interior of the leaf and sends to the exterior of the lower surface only the conidiophoric branches with the conidia (*see* Vol. II.) forming scabs like mould, which then dry up the leaves, thus causing paucity of sugar in the grapes and inferior and unsound wine. In Europe more than 100,000 tons of sulphur are used yearly to combat oidium, apart from the various polysulphides proposed during recent years. It is supposed that the sulphur acts on the oidium through formation of SO_2, which is in part already present in small quantity in the sulphur itself. Pollacci (1876) attributes the action of the sulphur to the formation of H_2S produced by lower organisms, while others now consider the principal effect to be due to the formation of small amounts of sulphuric acid.

Sulphur is employed as a cement, by melting it with iron filings and ammonium chloride; on cooling, this mixture expands and hermetically closes fissures and empty cavities when employed for fixing metal to stone, etc.; a good cement which quickly hardens very satisfactorily is also obtained by mixing 100 parts of cast-iron filings and turnings with 3 to 15 parts of sulphur, then adding 3 to 5 parts of ammonium chloride, moistening with water and mixing. When fused alone or with other substances, it is used for taking casts and impressions.

It is used medicinally for skin affections in the form of ointment or in baths, and also in conjunction with iodine for the treatment of other complaints.

It is also used in fire extinguishers, mostly mixed with 2 parts of sodium nitrate and about 4 per cent. of carbon.

COMMERCIAL VARIETIES OF SULPHUR. According to their origin there are various brands of commercial sulphur with varying fracture and colour. Amongst crude sulphurs there are recognised: (1) *Licata;* (2) *common Licata* or *good Licata f. m.* (mixed flowers); (3) *good Licata f. m.* or "*vantaggiata Licata uso,*" etc. Flowers of sulphur are sold as: *Solfo extra finissimo A* and *T* (*A* = Messrs. Albani, Pesaro; *T* = Messrs. Trevella, Catania), *solfo acido finissimo puro A, solfo sublimato V* (*V* = Messrs. Verderame, Licata), *sublimato extra impalpabile T,* (also *acido*), etc. Of winnowed and ground sulphur we have: *impalpable sulphur T, double refined T,* "*doppio ventilato*" *T and V, extra fine impalpable T,* "*molito raffinato*" *T, ventilato vergnasco T,* etc. The term *fuori miscela* (mixed flowers) refers to sulphur in whole loaves or in pieces, free from powder and heterogeneous particles.

The brands called "raffinate" (refined) vary in purity from 99 to 100 per cent.; the impurities are not more than 0·5 per cent., and the hygroscopic moisture is often less than 1 per cent. (sometimes only 0·04 per cent.). Sulphur marked "greggio" (crude) contains 3 to 10 per cent. of impurities.

STATISTICS, PRICES, AND POSITION OF THE SULPHUR INDUSTRY.[1] The production in Sicily and in other countries and the international trade in sulphur is shown in the table on page 211.

The Romagna produces from 20,000 to 30,000 tons of sulphur, and the Neapolitan district 20,000 to 25,000 tons.

Of the Sicilian sulphur from 140,000 to 150,000 tons are refined (partly ground and partly winnowed [*ventilato*]) in Italy, especially in Sicily; in 1908 204,240 tons of crude sulphur were exported from Italy in loaves and lumps to the value of £760,000 (in 1910, 212,850 tons, worth £820,000); 68,300 tons of ground sulphur to the value of £300,000 (in 1910, 74,100 tons, worth £346,800); 55,700 tons of refined sulphur to the value of £220,000 (the same in 1910); 1770 tons of flowers of sulphur, valued at £8840, and 8500 tons of coppered sulphur mixed with 3 per cent. of copper sulphate.

The *world's production* of sulphur (exclusive of 80,000 tons recovered from Leblanc soda residues) consisted up to 1900 to the extent of 95 per cent. of Sicilian sulphur, but in 1908 45 per cent. of the total production came from the United States. Other countries produce only minimal amounts: In 1900 Germany, Austria, and Russia produced from 1000 to 2000 tons each; Spain 6500 tons (in 1905, 12,500 tons from Albocete, Murcia, and Almeria); Portugal, 24,500 tons in 1909; France, 11,500, and Japan 35,000 tons in 1907 and 38,000 in 1909 (three-fourths from the island of Hokkaido).

The world's production was 809,000 tons in 1913.

In 1900–1901 84,000 tons of Sicilian sulphur were consumed on the Italian mainland, 99,000 in 1905, 60,000 in 1908, 50,000 in 1909, 63,200 in 1910, and 72,700 in 1911. The exportation amounted to 30,000 tons (in 1905 and 1911) to Germany, 104,000 tons (60,000 in 1907, 94,500 in 1908, and 113,000 in 1911) to France; in 1911 England, Belgium, Greece, Turkey, Sweden, Norway, Denmark, Austria, Russia, and Portugal each imported 12,000 to 25,000 tons.

Crude sulphur is despatched in sailing vessels from Porto Empedocle, Catania, and Licata.

---

[1] It is calculated that the deposits still unexploited in Sicily contain about fifty-five million tons of sulphur, and will be exhausted in about one hundred years.

It is now believed that the formation of the sulphur in the natural deposits in Sicily occupied about ten thousand years.

In commerce, for small consumers, the prices for sulphur are:

		£ s. d.	
Sulphur, refined, in loaves	about	5 12 0	per ton
„ „ „ rolls	„	6 8 0	„
„ double refined, ground and winnowed (*ventilato*) 75°–80° Chancel . . .	„	8 0 0	„
Flowers of sulphur	„	6 16 0	„
Precipitated sulphur for medicinal purposes (milk of sulphur or magister of sulphur)	„	£38–£40	„
Green commercial precipitated sulphur for rubber manufacture	„	£32	„

In large quantities the prices are from 10 to 20 per cent. lower f.o.b. Genoa. Thus, crude fused sulphur in loaves is sold at 72*s.* to 76*s.* per ton and ore with 40 per cent. of sulphur is valued at 8*s.* to 12*s.* per ton.

In 1914 a mining engineer in the Caltanisetta district calculated the cost price of a ton of sulphur at the mine quay as follows: labour to extract the mineral and administrative charges, 25*s.*; treatment of the mineral, 5*s.* 8*d.*; various materials (coal, timber, iron, lime, stone, gypsum, etc.), 5*s.* 3*d.*; general expenses, 4*s.* 4*d.*; rent of the mine (paid with sulphur), 10*s.* 3*d.*; transport to railway, 3*s.* 7*d.*, and from rail to port, 3*s.* 10*d.*; workmen's insurance, 1*s.* 7*d.*, and various expenses, 6*d.* Total cost of 1 ton of sulphur, £3.[1]

	SICILY				UNITED STATES		
Year	Production Tons	Price in Lire per Ton	Exportation Tons	Stock Tons	Production Tons	Importation Tons	Exportation Tons
Up to 1830	2,000,000	—	—	—	—	—	—
1830 to 1870	4,250,000	—	—	—	—	—	—
1870 to 1880	2,250,000	120	—	—	—	—	—
1870	180,000	—	—	—	—	—	—
1880	312,000	100	274,000	—	—	100,000	—
1885	377,200	83	279,000	—	—	—	—
1890	328,000	77	317,000	—	—	112,000	—
1895	353,000	(1892–95) 56[2] (1894)	364,417	250,000	—	99,200	—
1900	501,000	95	570,000	300,000	2,000	134,000	—
1901	548,000	95	—	310,000	—	175,000	—
1902	496,300	95	—	340,000	30,000	177,000	—
1903	527,000	96	—	361,000	137,292 (1904)	191,000	—
1905	537,000	95	456,000	462,000	218,677	84,300	—
1906	471,000	92	387,430	527,000	294,000	64,560	—
1907	446,000	91	345,000	546,000	312,000	28,073	14,500
1908	405,500	—	378,000	616,450	372,000	19,484	—
1909	402,350	—	365,000	648,000	241,500	26,900	37,000
1910	398,000	97	396,000	641,500	258,500	28,600	30,700
1911	366,000	—	447,600	540,000	268,500	24,250	28,100
1912	351,954	98·4	—	—	308,000	27,000	60,000
1913	347,588	99·4	—	—	—	—	—
1914	337,232	101·44	—	—	380,000	—	—

---

[1] The cost of production of sulphur per ton in 1890 has been estimated as follows (Ann. Agricoltura, 1890, 171): 6765 kilos of ore at 4*s.* 1*d.* per ton = 27·6*s.*; labour at the kilns, 3·44*s.*—total, 31·04*s.*; 200 kilos are due to the owner of the property, so that for the 31·04*s.* only 800 kilos of sulphur are obtained, and thus 1000 kilos of crude sulphur cost £1 18*s.* 10*d.* at the locality where it is obtained; to this must be added the cost of transport to the nearest port, 5*s.* A ton of sulphur thus costs £2 4*s.* in all to produce, to which must be added the cost of refining.

[2] In 1893 and 1894 there were revolutionary movements in Sicily due to misery and hunger, which should have found their explanation and extenuation in the above figures, but instead they were attributed to political movements and were repressed with bloodshed by the fierce and ignorant authorities.

In Sicily in 1897, after the prolonged crisis of the preceding years, which led to the abolition in 1896 of the export duty, yielding £120,000 per annum to the Government, the lot of the sulphur industry improved, more especially through the efforts of the Anglo-Sicilian Sulphur Company, which associated a large number of the producers of sulphur and regulated the sale rationally in such a manner that the sale prices rose from £2 8*s*. to £3 16*s*. 9*d*. per ton.

The Anglo-Sicilian Company continued to exist until 1906, but meanwhile a new and unforeseen circumstance arose on the horizon, namely, the intense exploitation of the important sulphur deposits of Louisiana by the Frasch process (*see below*). In 1905 the first consignments of American sulphur arrived at the port of Marseilles at very low prices, so that the Anglo-Sicilian Sulphur Company were obliged to come to an agreement with the Union Sulphur Company of New York, for one year, in order to prevent a fall of prices. Meanwhile the Italian Government sent the engineer, Baldacci, to Louisiana to study the threatening problem of American sulphur. Early in 1906 it was known with certainty that the American Company, though only four of its mines were working, would be able to throw on to the market a further 400,000 tons of sulphur per annum, at the following prices: 14*s*. 9*d*. per ton at the mine; 19*s*. 3*d*. at New Orleans; £1 6*s*. 4*d*. in the ports of New York, Boston, etc., and £1 11*s*. 7*d*. in European ports. On the other hand, the United States, which imported 191,000 tons in 1903, commenced appreciably to diminish their imports (*see* Table), and later to export large quantities.

Thus a very grave calamity menaced Sicily, and rendered imminent the economic ruin of many producers and works.

There were actually in Sicily in 1903 757 active sulphur mines, employing 37,000 operatives, of whom 8700 were hewers in the mines and the rest porters, 57 per cent. of the ore raised being still carried on the backs of these people. The average wages of the operatives were 1*s*. 7*d*. per day, and have increased but little in spite of the recent enhanced cost of living; in 1907 the number of operatives had decreased to 27,000, and in 1909 to 24,700; in 1909 80 small mines were closed and only 500 were still working, of which only six yielded more than 1000 tons of crude sulphur per annum.

In any case the whole Sicilian sulphur industry is still menaced with ruin if a more rational and economical method of sulphur extraction and of its sale is not found, and if the production is not limited. Meanwhile when the Anglo-Sicilian Sulphur Company came to an end, on July 15, 1906, the Government established by law the "Consorzio obbligatorio per l'industria solfifera siciliana," which is charged with the sale of the sulphur of all the Sicilian producers for twelve years.[1] Sulphur for agricultural use in Italy enjoys a

---

[1] The principal stipulations of the law of 1906 were as follows: (1) A monopoly of the sale of all Sicilian sulphur is granted to the Consorzio; (2) the Consorzio is empowered to limit the production of the individual proprietors in order not to be forced to sell sulphur at too low a price; (3) the Consorzio acquired 360,000 tons of sulphur accumulated by the Anglo-Sicilian Co. at a price of £2 7*s*. 2*d*. per ton, in return for the issue of bonds at 3·65 per cent., guaranteed by the State and redeemable in twelve years; (4) the Bank of Sicily is empowered to exceed, up to £400,000, the sum of £240,000 allowed in Article 30 of the law regulating that institution, for the emission of warrants to the credit of the sulphur deposited in the warehouses of the Consorzio.

The producers received in advance four-fifths of the value of the deposited sulphur. On the Council of the Consorzio the producers, the Chamber of Commerce, the Bank of Sicily, and the Government are represented, but, as happens so often in Italy through natural economic laws, the law has in this case again been of use to the local *camorra* and to illicit private interests. In fact, the power to regulate and diminish the production in order not to increase the already enormous stock was not enforced, and further production proceeded merrily, quite independently of the demand, as the producers were assured of four-fifths of the established price in advance, however high this might be. In 1907 the stock rose to 546,000 tons! Then the Bank of Sicily, in fear of an imminent financial disaster through the growing American competition, which might lead to a strong fall in prices, reduced the advance to three-fifths, because it was already liable for £400,000. They had, however, better have left it alone! The producers threatened revolution and the end of all things, and not succeeding in exciting the operatives, they suddenly diminished their wages and so forced them to unemployment and disorder. Their object was thus gained, and in October 1907 the Government authorised the Bank of Sicily to advance the four-fifths and raise their liabilities by a further £80,000. The appetite grows by eating, and though the production has been slightly reduced, the stock of sulphur rose in 1909 to 648,000 tons (*see* Statistical Table). The heads of the Consorzio freed themselves from all responsibility by resigning, and the Government ordered a Royal Commission in Sicily for the reorganisation of the Consorzio. Exceptional sales at lower prices were authorised in order to diminish the stock, and prices were fixed for the different qualities as a basis for the advances rebate of 5 per cent. Various other concessions were made diminishing the taxes with which the Sicilian sulphur industry is burdened. During 1908 and 1909 there was an agreement between the American company and the "Consortio Siciliana" limiting the regions of sale to two localities and thus avoiding a too rapid fall of prices.

EXTRACTION OF SULPHUR

NATIVE SULPHUR. This is found in large quantity in Sicily, principally on the southern watershed, from Etna to Sciacca, and more especially in the provinces of Caltanisetta and Girgenti, where it forms large deposits mixed with limestone or gypsum (up to 80 per cent. of sulphur). It is also found in Romagna (less abundantly), especially in the provinces of Forli, Rimini, and Cesena. Small deposits are also found in the Caucasus, Spain, Greece, and Japan. Important deposits are also worked in Louisiana, U.S.A. The new deposits worked in California contain up to 45 per cent. of sulphur, and large deposits occur also in the South American States.

Ores containing less than 10–15 per cent. of S (according to the depth) do not pay for working.

Solfatare are deposits in the ground of flowers of sulphur, formed by the interaction of gases which are still evolved from the craters of spent volcanoes, namely, fumes of sulphur and hydrogen sulphide (H_2S). The former burn to form sulphur dioxide (SO_2), and this reacts with H_2S with separation of all the sulphur, as explained by Dumas in 1830 :

$$2H_2S + SO_2 = 2H_2O + S_3.$$

The layer of sulphur in these solfatare is sometimes so shallow that it does not pay for extraction (at Pozzuoli), but it is sometimes 6 to 10 metres thick.

Solfare are layers of sulphur at varying depths below ground, and consist of a thick deposit of sulphur, probably formed by condensation of sulphur vapours coming from internal points of the earth's crust. Almost all the sulphur is to-day obtained from solfare.

Mottura explains the formation of sulphur in solfare by the decomposition of calcium sulphate by means of carbon, hydrocarbons, or organic matter, at high temperatures and pressures; the calcium sulphide (CaS) formed by this reaction, being soluble in water, would be carried to higher strata, and in contact with air and carbon dioxide would deposit the sulphur :

$$CaS + O + CO_2 = CaCO_3 + S.$$

The sulphur mines (solfare) are 50 to 100, and sometimes even 200 metres deep. They are penetrated by inclined galleries with a winding shaft. The ore is mined by *picconieri*, who are the workpeople engaged at the working face, and the *carusi*, who are children, carry the material to the surface on their backs.[1]

---

made to the producers. The mean price of sale for the various qualities was 74*s.* 10*d.* per ton in 1908, 77*s.* 6*d.* in 1909, 77*s.* 7*d.* in 1910, 78*s.* 8*d.* in 1912, 79*s.* 6*d.* in 1913 and 81*s.* 2*d.* in 1914. The European war has considerably increased the price of sulphur and the whole stock of 600,000 tons has been sold—mostly to Germany and Austria, to make sulphuric acid for the manufacture of explosives. The greed of the Italian speculators was stronger than their patriotism.

[1] In 1907 L. Borri reported that these operatives formed an organically degenerated body of people, deformed, with swollen thorax, head imbedded in the shoulders and the lower limbs compressed against the abdomen; the progenitors of these people were a strong and handsome race! The first labour law introduced (1902) was concerned with the women and girls—small girls of seven and eight years old, at work owing to the poverty of their parents—who were by this law prevented from carrying the ore from the galleries at the working face to the surface, up a steep slippery passage, roughly hewn in the rock; the ore was carried in loads of 30–50 kilos on the posterior thorax and the neck. These poor, ill-nourished *carusi* had to make twenty-five or thirty journeys a day, half-naked, bathed in sweat, covered with dust, with a closed lamp affixed to the top of the head, accompanying their steps with groans forced from them by their

Modern shafts have now also been sunk, especially in the deeper solfare, and the ore is then brought to the surface by mechanical means; the galleries are well ventilated and provided with suitable pumps to remove the water which accumulates.

The sulphur occurs in strata 10 to 15 metres thick, these being separated from those beneath by layers of limestone 15 to 20 metres deep. The shaft for the lift is sunk vertically in the limestone and is stopped before each sulphur stratum; when the latter is exhausted, the shaft is continued further down. The exhausted strata are gradually filled up with the residues left after extraction of the sulphur by fusion. The blocks of ore are often loosened by means of small mines of gunpowder or, occasionally, of dynamite.

The ores from the solfare are divided into three qualities: Rich ores with 30 to 40 per cent. of total S, yielding 20 to 25 per cent.; good ores with 20 to 35 per cent., yielding 15 to 20 per cent.; and ordinary ores containing 20 to 25 per cent. and yielding 10 to 15 per cent. of sulphur; ores with 10 to 12 per cent. of sulphur do not ordinarily pay for working. A cu. metre of the ore weighs 1000 to 1200 kilos.

Until 1850 the sulphur was extracted by fusion, by burning the ore in small heaps called *calcarelli*, or small calcaroni, of about 2½ metres diameter. By this system only 20 to 30 per cent. of the total sulphur was extracted; the rest was burnt to sulphur dioxide, which polluted the air and caused enormous damage both to the health of the populace and to vegetation.

The methods of extraction were then much improved, and after 1850 the system was started of collecting the ore into much larger heaps covered outside with earth or ash from the already treated ore (called *ginisi*).

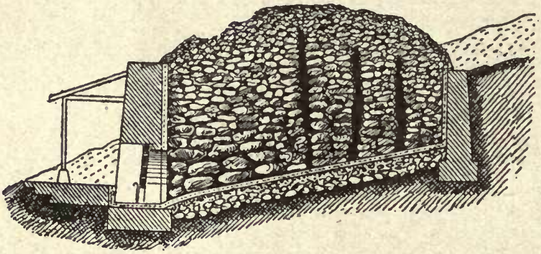


FIG. 73.

These large heaps are called *calcaroni* (Fig. 73). They hold up to 2000 cu. metres of ore, containing not less than 15 per cent. of sulphur, and the combustion lasts from one to two months. A third of the sulphur is consumed as fuel.

The calcaroni are built up in places sheltered from the wind in a circular excavation in the ground, 10 to 20 metres in diameter and 2 to 3 metres deep. The floor is well beaten down and is inclined towards one point where the fused sulphur collects.

Large lumps of ore are placed at the bottom and are arranged in diminishing size upwards to a height of 4 to 5 metres and are then covered with material which has already been treated. The sulphur is set on fire from the top by introducing lighted wood through channels left for this purpose; the heat slowly spreads, and melts all the sulphur, which collects at the base in boxes of moist wood where it solidifies to loaves of 50 to 60 kilos weight, forming crude fused sulphur which is very impure and of a dark colour.

---

heavy labour. This overwork weakens the muscular resistance and that of the bones; the lungs, heart, and blood-vessels are unable to recover rapidly from its effects, and the flower of youth soon succumbs. The *caruso* of to-day will be the hewer (*picconiero*) of to-morrow! The sad economic conditions of these people have urged these same operatives to implore the Government to suspend the law preventing the employment of women and girls, as owing to the low wages of these *carusi* this is said to be indispensable if their families are not to die of hunger! The proprietors have supported this demand, and the Government . . . piously concedes it!

Many of the hewers and carriers are affected with anchylostomiasis, which is an infection of the blood—specific to these miners—that destroys the red corpuscles and causes a peculiar anæmia resulting in deathly pallor and a slow, but continuous decay of the organism.

Spontaneous fires of the sulphur in the mine galleries are not infrequent and often cause grievous loss of life by suffocation. Means of rescue are in many cases defective.

The maximum yield obtained in the calcaroni is about 60 per cent. of the total sulphur (for an ore containing 25 per cent. of sulphur, 70 per cent. of limestone, and 5 per cent. of moisture), whilst theoretically the yield should be about 85 per cent., 15 to 20 per cent. of the sulphur being burnt in order to raise the temperature of the ore sufficiently for the fusion of the remainder.

A more rational manner of working, with a better yield, is attained with the regenerative furnaces patented by Robert Gill in 1880, in which the heating is performed in closed chambers of brickwork, holding up to 30 cu. metres of ore. A yield of 65 per cent. of the total sulphur can thus be obtained without polluting the air and damaging the neighbourhood. In this case also the heating takes place at the expense of the sulphur which burns.

These regenerative furnaces (Fig. 74) are formed of two large brickwork chambers, both communicating with the same chimney in such a manner that combustion can be readily regulated. When combustion is finished in one chamber it is commenced in the other, so that there is continuous working. With the two chambers of such a furnace forty-five to ninety charges can be worked per annum. The charge of ore is arranged as in the calcaroni, with the larger lumps below and finer material at the top, so that the molten sulphur may readily find its way to the bottom, where it collects on a floor which is gently inclined and is sometimes separated from the ore by means of a double floor.

These furnaces have been still further improved by replacing them by circular furnaces with four or six chambers, which permit of the better utilisation of the heat of combustion emitted by them in turn. In this way yields of more than 70 per cent. of the total sulphur have been obtained. Of late years the Sanfilippo furnaces have also come to the front and allow of a still better yield and of the utilisation of poor ores, as the chambers of the furnace are traversed by numerous perforated vertical channels which allow the access of air to all points of the mass to be regulated.

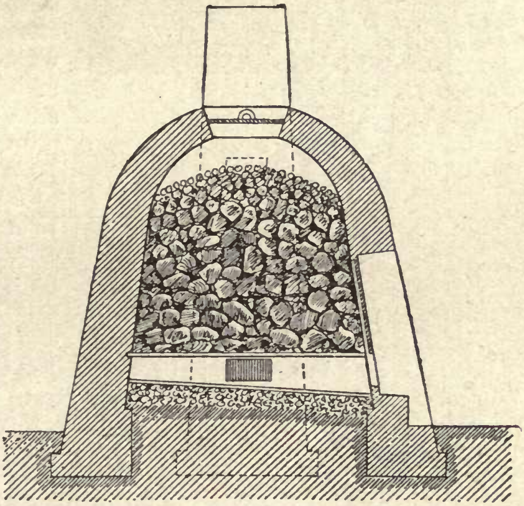


FIG. 74.

Sulphur is also extracted from its ores by making use of its easy fusibility under the action of superheated steam at 3½ to 4½ atmospheres pressure.

This principle was proposed by Payen and by Gill in 1867; the first apparatus was constructed by Thomas in 1869 and applied by Gill after 1884. A final improvement, indicated in a patent of 1891, rendered the use of this apparatus possible.

The Thomas steam extractors consist of large horizontal iron cylinders, encased in wood, 6 metres long and 80 to 100 cms. in diameter. Fig. 75 shows a portion of such a cylinder. Small wagons with perforated bottoms are charged with the ore and run on the rails, *S*, inside the cylinder; the door is firmly closed after charging, and superheated steam at 130° is admitted by the cock, *C*, which is closed when steam only escapes. The molten sulphur collects in the receiver, *g*, carried in the small car, *B*, and connected with the main extractor by a steam-tight joint; this can be removed when the extraction is complete. The steam is discharged under pressure from the valve, *h*, into another similar apparatus and a fresh batch of ore is then treated. Eight to twelve batches of four to five tons each can be treated daily.

In order to treat 24 tons of 25 per cent. ore in twenty-four hours 600 kilos of coal (£1) are required, and four tons of sulphur are obtained. If the same quantity of ore is treated in calcaroni at least a ton of sulphur is lost, this costing more than the coal. Extraction with steam gives a yield of 60 to 80 per cent. of the total sulphur, but requires greater expenses for plant and for fuel (which is rather dear in Sicily), so that this method cannot be extended in the island; further, if the ore is powdery the sulphur forms a paste with it, whilst if it is porous it retains part of the sulphur, the residual slag containing 8 to 14 per cent. of sulphur. In 1901 91 steam extractors were at work in Sicily. Replacement of the steam by hot air (tried by G. Rocasolano in Spain in 1910) does not give good results, while sometimes the sulphur ignites (at 250°). Dubreuill's process of extracting sulphur by means of a hot saturated calcium chloride solution is not satisfactory.

G. Rocasolano (1910) obtained good results with a battery of inclined wide iron tubes heated with hot air. The ore is loaded into the tubes, which, at the bottom, either dip into a vessel full of water or communicate with a chamber in which flowers of sulphur are formed. The charge of each tube is 650 kilos of ore, and the yield of sulphur exceeds 90 per cent.

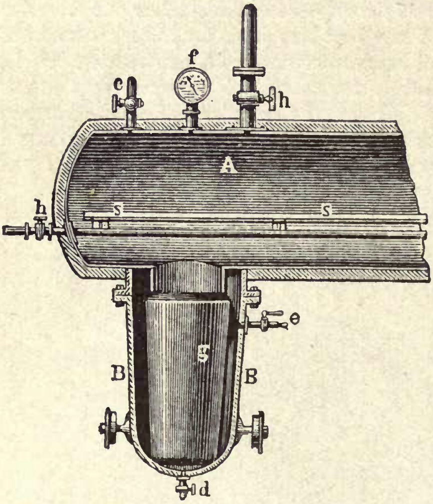


Fig. 75.

Of the sulphur produced in Sicily in 1891 75 per cent. was obtained in calcaroni, 17 per cent. in regenerative furnaces, and 8 per cent. by steam extraction. In 1903 only 32 per cent. was obtained in calcaroni, 55 per cent. in regenerative furnaces, and 13 per cent. in steam extractors. In 1906 the proportion obtained from regenerative furnaces rose to 66 per cent.

In Romagna, the ore is mixed with bituminous substances and if burnt in calcaroni would give a dark product. In small quantities it is treated by distillation in numerous "*pignatti d'argilla*" (clay retorts) of 20 litres capacity heated in a suitable furnace called a "*galera*." The sulphur vapours are condensed outside the furnace in other *pignatti*.

For larger production "*doppioni*" are used (Fig. 76), consisting of eight cast-iron retorts, 1 metre high and 0·5 metre in diameter, obliquely arranged in a furnace. The sulphur vapours pass through the tube *j* into a condenser, *h*, common to two retorts, and the liquid sulphur so obtained collects in receivers, *i*, which are kept hot by the furnace gases passing along the flue, *K*. It takes twelve hours to treat a batch of ore in a set of eight retorts. Each retort takes 150 kilos of ore per twelve hours. The "*doppioni*" are not used for production on the large scale, as production is too expensive on account of the small output, high cost of plant, and rapid wear of the retorts.

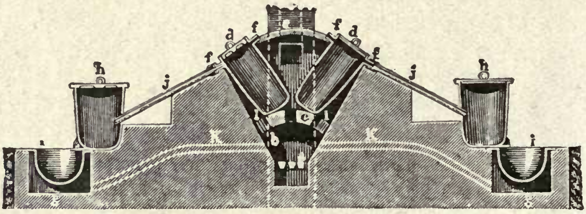


Fig. 76.

At Latera, near Rome, good results have been obtained from a poor ore (13 per cent. S) by extraction with steam. A special apparatus was used, devised by Gritti, and patented by the Compagnia francese delle cave di Latera. For some years, however, the extraction of sulphur at Latera has ceased.

The extraction of sulphur with carbon bisulphide (Condy-Bollmann method) has been tried at Naples and at Swoszowice with poor ores (15 per cent.), and 99 per cent. of the sulphur was obtained. For special reasons the extraction with carbon bisulphide at Naples was not continued.

New deposits of sulphur have recently been found in the Caucasus, and it has been calculated that they are capable of yielding, altogether, nine million tons of sulphur; at present this is burnt on the spot for the direct production of sulphuric acid.

A proposal has been made to extract it by Petcanoff's method, as follows: The ore is thrown into brickwork chambers, which can be hermetically closed, provided with a false bottom, and water is added which fills the interstices in the ore; the whole is then heated with superheated steam, which causes the sulphur to melt and collect in the pure state on the bottom.

At Charles Lake, Louisiana, the sulphur deposits have been known since 1868, and the sulphur has recently been extracted from fairly deep strata by H. Frasch's method (the first patent, of 1891, gave poor results, but U.S. patent No. 800,127 of 1905 has been successfully used) without sinking shafts; by this method it is possible to pass through layers of the hardest rock to a depth of 240 metres, where there are compact deposits of sulphur, 30 to 40 metres thick and fairly pure. Frasch sinks a well, 25 cms. in diameter, just as in boring for petroleum, lined with an iron tube, until he arrives at the rock under which lies the sulphur. In this tube are suitably fixed two other concentric tubes, lined with aluminium and of 7·5 and 3·5 cms. diameter, which are driven into the sulphur layer. The outer tube is then surrounded with superheated water at six atmospheres pressure (155° temp.) which melts the sulphur and forces it to ascend the middle tube as a liquid of density 2; it is here surrounded by hot air at 130° C. The molten sulphur rises to a certain height in the tube and attempts were first made to extract it by a pump with aluminium valves, which resisted the corrosive action of the sulphur but were unable to support the strokes of the pistons. This difficulty was ingeniously surmounted by introducing through the central tube a current of compressed air which so strongly emulsified the column of molten sulphur that it was rendered lighter and rose to the surface without a pump. Thus the principles of the Kühlmann emulsifier and the Mammoth pump, already used for raising acids and other liquids, were here applied together (*see* illustration to the chapter on Sulphuric Acid). At the surface the fused sulphur is collected in large wooden boxes where it solidifies, and the water and hot air are utilised again.

In 1896 Frasch extracted by his method 2100 tons of sulphur. He afterwards increased his plant and formed in 1902 the Union Sulphur Company of New York, which obtained 100 tons of sulphur per day by this process; by the end of 1903 the production had risen to 550 tons daily; in 1904 it rose to 800 tons, and in 1905, with four batteries of boreholes and 600 workmen, the daily production was about 1500 tons. In 1909 the United States exported 39,000 tons of sulphur and in 1913 sold in Europe more than 50,000 tons, cheaper and purer than Sicilian sulphur; in 1911 they imported only 24,000 tons, 16,000 from Japan and 8000 from Italy. At first about 1000 kilos of coal were used for boilers, etc., per 300 kilos of sulphur, but to-day this has been advantageously replaced by petroleum. In 1911 there were at work 130 boilers of 150 to 300 h.p. each, divided into batteries of 15 to 20 boilers heated with petroleum residues, 700 barrels (1 barrel = 159 litres) being consumed by each battery per day. The annual consumption of petroleum residues amounted to a million barrels; the amount of water used was 26,000 cu. metres per day, this being obtained from wells.

By simply melting the extracted sulphur with steam in iron boilers a product of 99 to 99·6 per cent. purity is obtained with a loss of only 1·5 per cent. It is easily understood that the Frasch process is applicable only to very pure sulphur deposits.

The sulphur deposits of Louisiana have been estimated to contain forty million tons, and important surface deposits of sulphur of volcanic origin (solfatare) which have not yet been exploited are found at Kadiak and generally in the volcanic islands of Alaska. Large deposits occur also at Riviera Bragos, in the Southern States of America.

A special and rather complicated method has been suggested by Stickney for the recovery of sulphur from iron pyrites; the ore moves automatically in a cylindrical furnace, and is heated with either water-gas, petroleum, coal, or steam. The sulphur vapours are condensed by a spray of saline solution. Large scale trials made on the basis of results obtained by W. A. Hall in France and England and then in America (1913) with MacDougal mechanical furnaces showed that every ton of pyrites passing through a sieve of 3·5 mm. mesh and distilled at about 800° requires a consumption of 75 litres of petroleum residues; the mass remaining contains 5·3 per cent. of sulphur and the vapour and gas 0·3 per cent. of SO_2. The first sulphur atom of FeS_2 distils at 700°.

Small quantities of sulphur are also obtained, mixed with Laming's material, in the purification of coal-gas, and may be removed by extraction with carbon bisulphide.

The recovery of sulphur from the residues of the Leblanc soda industry is to-day of great importance. If all these residues were worked up by Chance's method, employing chimney gases (CO_2), 80,000 tons of sulphur would be obtained per annum. At present more than 40,000 tons are so obtained (*see* Soda, Part III), and can be profitably sold when the market price of Sicilian sulphur exceeds 48*s*. per ton.

REFINING OF SULPHUR. The first subliming plant was constructed by Michel at Marseilles in 1805 and improved by Lamy in 1844. A charge of 800 kilos of sulphur is heated in the pan, *D* (Fig. 77), where it melts and passes through the tube *F* into the iron retort, *B*, which is 1·5 metres long and 0·5 metre in diameter, and holds 300 kilos of sulphur. This is heated directly by the hearth, *A*, and the fire-gases rise through the flue, *C*, and heat the pan, *D*. When distillation from one retort is almost finished, the other is heated, the first being meanwhile shut off by closing the damper, *I′*, and then recharged. The sulphur vapours condense in the chamber, *G*, which has a volume of 80 cu. metres.

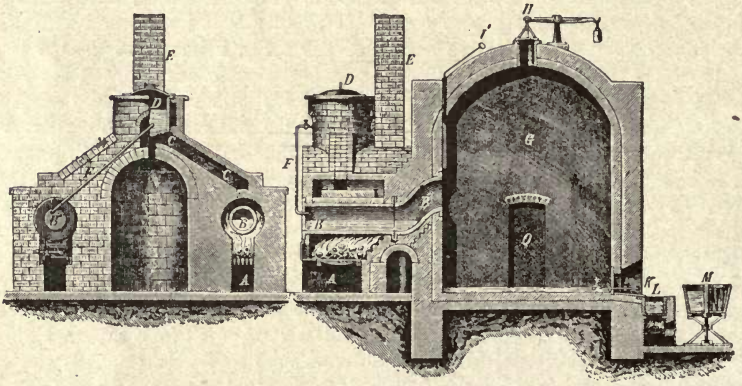


FIG. 77.

The distillation of the contents of each cylinder takes four hours, and from the two cylinders 1·8 tons of sulphur are obtained in twenty-four hours. If the condensing chamber is kept at a temperature above 114° molten sulphur collects on the floor, flows into the receiver, *L*, and is poured into the moulds, *M*, where it solidifies. If the temperature in the condensing chamber is below 100°, flowers of sulphur are formed, and in this case only 300 kilos are produced per day.

The method of Dujardin, who replaces the Lamy retorts by shallow retorts, is more rational, and only 2·5 per cent. of the sulphur is then lost. In twenty-four hours 3·6 tons of sulphur are obtained, using 0·5 ton of coal.

Much sulphur is refined at Marseilles and Antwerp, but a considerable quantity is also refined in Germany and Italy, especially in Romagna and Catania.

In order to decrease the losses in preparing flowers of sulphur, the use of inert gases such as N, CO_2, etc., instead of air in the condensing chamber, has been proposed.

N. O. Witt (German patent No. 186,332 of 1905) avoids the occurrence of molten sulphur with the flowers of sulphur by pulverising the molten sulphur by means of a superheated steam injector. H. Köhler obtains very fine sulphur (German patent No. 192,815) by fusing together equal weights of sulphur and naphthalene, distilling the mixture, and dissolving the naphthalene with a solvent; the precipitated sulphur thus obtained exhibits marked disinfectant properties.

Ground Sulphur. Formerly in Sicily the flowers of sulphur were simply sieved, but the product was only slightly adhesive to the vine-leaves. To-day the crude sulphur, melted and cast into loaves, is refined in the Sicilian ports by being remelted and transformed into flowers of sulphur, or is ground between millstones and the product passed through silken sieves, of 170 meshes to the inch. Sometimes the sulphur catches fire during grinding, but is easily extinguished with damp sacking. Seventy per cent. of this sulphur adheres to the foliage of the vine.

Winnowed Sulphur (*solfo ventilato*) is much superior for viticultural purposes, as it is more adhesive to the foliage. It was first prepared by Dr. A. Walter, at Bagnoli, near Naples, and contains 90 to 95 per cent. of fine adherent sulphur. Lumps of refined sulphur are placed at the bottom of a conical stone vessel in which a vertical millstone revolves. During the grinding a continuous current of air from powerful fans is introduced at the bottom of the apparatus. The finest sulphur is thus carried to the farthest points of the large closed chamber in which the operation is conducted. In order to allow the air to escape, there are windows covered with large sheets of cloth which retain the sulphur whilst allowing the air to pass. Each mill consumes 2 h.p., and yields 1 to 1·5 tons of winnowed sulphur per twenty-four hours.

Sometimes the very finely divided sulphur explodes with the oxygen of the air. Air containing little oxygen has therefore been suggested for this purpose, and is easily obtained by passing ordinary air over a layer of glowing charcoal; furnace gases may also be employed (Delilla, Ital. Pat. 51,474).

The firm of Walier and Tremwella in Naples and Catania alone produced 5000 tons of winnowed sulphur in 1890. This product is also manufactured in Romagna, Lombardy, and Piedmont. This sulphur has a pale yellow colour, similar to that of precipitated sulphur, and contains less than 0·5 per cent. of ash. The degree of fineness is determined by Chancel's method.[1]

---

[1] *Analysis of sulphur.* Chancel's sulphurimeter is used for determining the *fineness;* this consists of a glass cylinder, closed below, 23 cms. long, 12·68 mm. in diameter, and provided with a ground glass stopper. A volume of 25 c.c. is divided into 100 parts, which indicate Chancel degrees of fineness. The apparatus is constructed by J. Greiner, Monaco. The sample to be examined is first passed through a sieve of 1 sq. mm. mesh to break up the lumps, and precisely 5 grms. are then weighed into the apparatus, which is filled up with pure ether, free from alcohol (distilled over metallic sodium), to 1 cm. above the 100 mark, at a temperature of 17·5° C. The whole is then vigorously shaken vertically for thirty seconds and the apparatus suspended in a vessel of water at 17·5° without allowing it to touch the sides or bottom of the vessel, as any impact alters the results. The sulphur settles and the ether clears. When the layer of sulphur does not further decrease in the course of a few minutes a reading of its height is taken. The finer the sulphur the larger will be this reading. The shaking is repeated and the mean of four readings taken; this series of readings is then repeated with another 5-grm. sample of sulphur, and the mean of the two results is taken (H. Fresenius and P. Beck, 1903). Commercially there is an allowance of 5°. Sulphur of 40°–45° and also of 80°–85° Chancel is sold.

The *mineral impurities* (*ash*) are determined by burning 10 grms. in a tared porcelain capsule and weighing the residue.

Moisture is determined on a 100-grm. sample, after powdering and rapidly weighing, by heating for some hours in an oven at 100°; it is weighed after cooling in a desiccator.

Arsenic is tested for qualitatively by treating 1 grm. of sulphur with 15 drops of ammonia and 2 c.c. of water; after half an hour the liquid is filtered off and 30 drops of hydrochloric acid and 15 drops of oxalic acid solution added; a strip of polished brass is then immersed in the liquid, which is heated to 60°–100°. In presence of arsenic the brass quickly acquires a grey or black colour. The quantitative determination of arsenic is carried out by Schöppi's method, which will not be described here.

The *specific gravity* is determined with Schumann's volumeter.

Selenium is tested for by melting a little of the sulphur with potassium nitrate, then dissolving

SELENIUM : Se, 79.2

This element is rare, and is mainly found in certain Bohemian and Swedish pyrites. These pyrites are burnt in sulphuric acid works and the selenium is then found in the dust-chambers and in the mud of the lead chambers.

It has also been found in the lava of Vesuvius and in the island of Lipari; some is also produced in the Argentine and the United States, where it is obtained from the anodic sludge of the electrolytic copper refineries.

It was first discovered by Berzelius in 1817 in the mud of the lead chambers of a works at Gripsholm. It is extracted by treating the mud with a concentrated solution of potassium cyanide; the selenium is precipitated from the filtrate with HCl. It is then collected, oxidised with nitric acid, and evaporated, when solid selenium dioxide (SeO_2) remains, and is purified by sublimation. This oxide is reduced to metallic selenium by an aqueous solution of SO_2.

A. Koch has recently obtained good results (Ger. Pat. 167,457, Dec. 1903) by treating the lead chamber mud (consisting of lead sulphate and free selenium) at moderate temperatures with moderately concentrated sulphuric acid and potassium permanganate; sodium chloride is then added and the solution diluted and filtered. The selenium is then precipitated from the filtrate with sulphur dioxide.

PROPERTIES. Selenium melts at 217° (the variety in red crystals at 170°–180°) and boils at 665°, forming dark yellow vapours, the density of which diminishes up to temperatures of 1400°, when it consists entirely of diatomic molecules Se_2. It burns in the air with a bluish-red flame to form SeO_2, with an odour of rotten radishes. When heated with carbon, it yields red vapours of disagreeable odour.

It dissolves in strong sulphuric acid with a green colour, reacting according to the following equation:

$$Se + 2H_2SO_4 = 2SO_2 + SeO_2 + 2H_2O.$$

Sodium selenite is coming into use for determining whether a given medium is sterile or contains bacteria; in the latter case a noticeable amount of reduction takes place, and can be confirmed by the use of potassium tellurite (Gosio).

Selenium can exist, like sulphur, in various allotropic forms: amorphous selenium (by reducing SeO_2 with SO_2) is a red-brown powder of sp. gr. 4·26, soluble in carbon disulphide, from which it separates in small crystals of sp. gr. 4·50. A solution of potassium selenide on standing in the air deposits black scaly crystals of sp. gr. 4·80, isomorphous with sulphur, and insoluble in carbon disulphide. When rapidly cooled, molten selenium is transformed into a vitreous amorphous mass, black in colour, of sp. gr. 4·28, soluble in carbon disulphide; on cooling slowly, on the contrary, a crystalline mass is obtained, insoluble in carbon disulphide, of sp. gr. 4·80. When amorphous selenium is heated to about 100°, its temperature suddenly and spontaneously rises to over 200°, and it is transformed into a dark greyish, metallic, crystalline substance of sp. gr. 4·8, insoluble in carbon disulphide and a good conductor of heat and electricity, as is that obtained on slowly cooling molten selenium; on exposure to light the one form is transformed into the other. According to Coste (1910) only three forms of selenium exist at the ordinary temperature, namely: (1) vitreous, red selenium, of sp. gr. 4·30, obtained by precipitation; (2) crystalline red selenium, of sp. gr. 4·45, which melts at 144° and solidifies, changing into (3) metallic selenium, which melts at 219°, has the sp. gr. 4·80, and forms more easily in presence of traces of impurities. The study of the various allotropic forms of selenium has lately been pursued with much activity on account of important applications which are expected.

---

the mass in hydrochloric acid and treating with sulphurous acid, which precipitates the selenium as a red powder.

In order to distinguish molten sulphur from flowers of sulphur, it is only necessary to remember that the former is completely soluble in carbon bisulphide, in which the latter is mainly insoluble; the percentage of flowers of sulphur may be determined by means of Chancel's sulphurimeter, carbon bisulphide being used in place of ether—the Chancel degrees then give directly the percentage of insoluble sulphur in the sample.

Amorphous selenium is a bad conductor of heat and electricity, whilst crystalline selenium is a good conductor, and its conductivity increases when it is illuminated, and with the intensity of the illumination; this sensitiveness to light is very great, but is retained only for a short time, a fact which has greatly hindered any wide practical application of this most interesting property. Even traces of contamination with certain metals influence this special behaviour of selenium very greatly, and also after illumination the original electrical resistance is only slowly regained (after twenty-four hours), any practical application being thus rendered still more difficult. It has recently been found that the sensitiveness and its duration are increased if the selenium is heated to 200° in a dry atmosphere free from oxygen, and is then allowed to cool and crystallise slowly; also the addition of 0·1 to 0·5 per cent. of silver, and of other catalysers, increases the sensitiveness; a method is still needed of protecting active selenium from moisture (R. Marc, 1907).

The activity of selenium is not due to chemical action and has nothing to do with heat effects, as it still persists at the temperature of liquid air (— 190°), but is strictly connected with the action of light, which perhaps causes the transformation of one allotropic form into another, with alteration of density and probable formation of free ions or electrons, which are good conductors of the electric current.

In 1886 Graham Bell (the inventor of the telephone) succeeded in producing with the aid of selenium a wireless telephone, for transmitting sounds over a short distance (radiophone); the method was based on the observations of W. Smith in 1873. In 1904 E. Ruhmer, in Berlin, obtained much more important results by applying selenium to the speaking arc, discovered by Simon in Göttingen in 1898: If in a circuit containing an arc lamp a secondary coil is interposed, while the primary circuit is connected with a telephone transmitter, the light of the arc will be influenced by sounds which impinge on the transmitter, thus varying the intensity of the light; this is the speaking arc. A telephone receiver of which the microphone is connected with selenium reveals these oscillations of light, reproducing the sounds which influence the arc, and in this manner E. Ruhmer was able to speak at a distance of sixteen kilometres with his wireless telephone.

It is clear that the distance could not be very great, as in wireless telegraphy, as the electric arc and the telephone receiver had to be in the same straight line—in fact, had to be within sight of one another.

Photographic transmissions are to-day sent over large distances by using the circuit of Duddell and Poulsen, which produces continuous oscillations of high frequency (500,000 to 600,000 electromagnetic oscillations per second) capable of being received at a syntonic station, that is, one with oscillations of the same period.

Commercial selenium powder costs £5 12*s.* per kilo, and is used for producing a red colour in porcelain and glass;[1] as sublimed powder it costs £8, and in small rods £6 per kilo. In 1911 5000 kilos of selenium were obtained (for colouring glass) from the anodic sludge of electrolytic copper plants.

TELLURIUM : Te, 127.5

This element is not abundant in nature; it is found in the metallic state and mixed with gold, silver, lead, and bismuth, especially in Transylvania and in the Russian gold mines in the Altai Mountains. It is also found in the volcanic formations of the Lipari Islands. It was discovered first by Müller Edler von Reichenstein in 1782 in a gold ore and then in 1798 by Klaproth, who gave it its name; in the pure crystalline state it was obtained later by Priwoznik.

Tellurium is separated by sulphurous acid from solutions of tellurous acid as a black powder, of sp. gr. 5·9. When fused it has a silvery white, metallic appearance and is a good conductor of heat and electricity. It crystallises in rhombohedra of sp. gr. 6·4, melts at 452°, and boils at 1280°,

---

[1] P. Fenaroli (1913) has investigated the coloration of glass by selenium. Both the white and the red colorations are due to colloidal selenium and the red glasses tend to become turbid during cooling owing to the formation of selenides and selenites.

forming simple molecules of Te_2, even at 1400° to 1700°. The atomic weight was believed to be 128, but according to the periodic system it should be less than that of iodine (126·9), and Brauner actually found it to be 125; the latest and most exact work (Staudenmaier, 1895) brings us back, however, to the atomic weight 127·5.

Some gold ores contain tellurium. To obtain this element these ores are heated in cast-iron vessels with strong sulphuric acid; the gold and silica remain undissolved; the liquid is concentrated and then treated with boiling water and with 10 to 15 per cent. of HCl to precipitate the silver.

It is then filtered into lead-lined vats and treated with gaseous SO_2 from cylinders of the liquefied gas (70 to 100 grms. of SO_2 per litre of the solution of tellurium); this precipitates tellurium of 75 to 80 per cent. purity (without selenium) and it can then be purified, yielding a 95 to 97 per cent. product. The remaining mother-liquors contain Cu, Pb, Sb, etc.

Outside the laboratory tellurium has not yet received any important application, but experiments are always in progress to find a use for it in medicine, for colouring porcelain, or for electrotechnical purposes. Attempts have been made to use it in place of sulphur in the manufacture of ultramarine, but owing to the impurities it always contains (especially copper) good results have not been obtained. Gosio has employed potassium tellurite in order to discover whether substances are properly sterilised, as it is reduced by the action of bacteria, with production of a coloration. Pure tellurium powder costs £18 per kilo, and when cast into sticks £22 per kilo.

HYDROGEN COMPOUNDS OF THE GROUP : O, S, Se, Te

At high temperatures these four elements combine with hydrogen to form compounds which have the general formula $X''H_2$, and at still higher temperatures are decomposed into their components. Whereas water (H_2O), however, is a liquid and non-poisonous, the hydrogen compounds of the other elements are gaseous and poisonous to the human system. Further, water is a strongly exothermic compound, whilst hydrogen sulphide, H_2S, is but weakly exothermic (2600 cals.), and hydrogen selenide and telluride are endothermic. The aqueous solutions of the three last compounds are decomposed by oxygen and still more easily by the halogens, forming oxides.

WATER : H_2O

This compound is found in nature as meteoric, spring, river, lake, and sea water.

Water is found very abundantly in nature and covers three-quarters of the earth's surface;[1] a very large quantity is also present as vapour in the atmosphere, from which it separates continually in the forms of fog, dew, rain, snow, hail, etc., which are all forms of meteoric water. More meteoric water falls in the tropics and in the neighbourhood of the sea than in more northern countries; more falls in the mountains than on the plains, and more in summer than in winter.[2]

On investigation of the amount of water which falls in various parts of the earth's surface, measured in depth of water by means of suitable rain-gauges, it is found that the average rainfall in Petrograd is 45 cms. per year; in Berlin it is 57, in Rome 78, in Genoa 118, in Milan 60 to 100, at Tolmezza (in the Alps in the Province of Udine) 244, and at Bergen (Norway) 225 cms. per year.

The amount of water which falls annually varies very much: thus the mean annual rainfall in Frankfort during thirty years was 60 cm., but only 36 cm. fell in 1864 and

---

[1] In 1913 Halbfass calculated the approximate amount of water on the globe, in billions of tons, to be: oceans, 1,300,000,000; polar ice, 3,500,000; lakes and pools, 3,500,000; rivers, 50,000; marshes, 6000; snow, 250,000; clouds and atmospheric vapour, 12,300.

[2] *Translator's note.*—This last remark applies only to certain portions of the earth's surface.

140 cm. in 1867; hence the great difficulty of establishing rigorous meteorological laws. About half the rain water evaporates almost immediately into the atmosphere, whilst the other half descends under the action of gravitation into the lower layers of the earth's crust and reappears as springs, rivers, and in the sea.

Large pine forests appear to increase the quantity of rain, and certainly cause it to be better distributed over the ground; they also act advantageously by hindering avalanches and inundations during storms, as the leaves and the vast network of roots retain the water.[1]

Meteoric water is of the greatest importance in the economy of nature, because it supplies the water necessary to man for domestic and sanitary purposes and for drinking; it supplies water for agriculture, and is also important as a source of energy, as it furnishes a means of utilising indirectly the solar heat which is apparently dispersed over those three-quarters of the globe (seas and lakes) where there is no vegetation and no crops to ripen. This solar heat is not in fact lost, but serves to transform part of the water at the surface of the seas, lakes, and rivers into vapour which is deposited in the form of rain on the plains and mountains and returns to the sea, furnishing motive power for innumerable enterprises during this cycle and producing work and wealth everywhere.

Meteoric water contains in solution the component gases of the air in the ratio of their solubilities. One litre of rain water contains in winter 32 c.c. of gas (air) and in summer 25 c.c., containing 27 per cent. O, 64·2 per cent. N, and 8·8 per cent. CO_2; it also contains traces of NH_3, HNO_3, HNO_2, H_2SO_4, and during storms also a little hydrogen peroxide.

The following is the average composition of rain water, deduced from that of seventy samples collected in England: total solids per litre 39·5 mgrms., ammonia from 0·2 to 5 mgrms., N_2O_5 from 0·18 to 2·7 mgrms. or even more.

The rise in level of the water of the subsoil which occurs in certain rainy years is often characterised by pollution of the water of wells and by increase in the number of cases of typhus.

Meteoric water dissolves various substances during its infiltration through the ground, including CO_2, which in turn forms bicarbonates by dissolving the salts of Mg, Fe, Mn, Ca, etc.

PHYSICAL PROPERTIES OF WATER. Water solidifies at 0°, or below this temperature if completely undisturbed; before solidifying at 0° it has a density of 0·99987.

In vacuo, or when covered with a layer of oil, it solidifies at — 10°, or even at — 20°. Aerated water may be cooled to some degrees below zero without solidifying, and if water free from air is added, this alone solidifies. Some dissolved substances retard solidification very much, for instance, ether and various salts (*see below*, Freezing Mixtures).

On cooling, water continues to diminish in volume until 4° is reached, when one litre of water weighs 1000 grms., whilst at 0°, before freezing, it weighs only 999·8 grms.; during transformation into ice great dilatation takes

---

[1] Ill-considered deforestation in the past has deprived large regions of water reservoirs and has given rise to continuous lack of temperature equilibrium; rain occurs when it is not required, as well as excessive and prolonged frosts and violent winds which destroy vegetation and cause immense damage. Woods prevent damage from floods because they partly hold back the rain water and restore it slowly to the brooks and to the atmosphere; they cause less torrential and more frequent rain by maintaining in their neighbourhood a fresher zone which facilitates condensation of the moisture of the atmosphere. (*Translator's note.*—More especially on account of the enormous quantities of moisture absorbed by the roots and restored to the atmosphere by the leaves in the processes of plant metabolism.)

In the island of Malta, since extensive deforestation to make room for cotton cultivation, the rainfall has been insufficient, sometimes for three years on end. In St. Helena, on the contrary, the large afforestations have increased the rainfall to double the amount which fell in the time of Napoleon.

Torrential rains remove the most useful components of the soil very easily, and the mountains and hills are soon denuded until bare rocks remain (in absence of trees). In Italy in 1870 there were 5,200,000 hectares of forest, but in 1905 these had been reduced to 4,000,000 hectares, *i. e.*, 16 per cent. of the total cultivated area, whereas in France the percentage is 19, in Germany 28, and in Austria 30. In 1910 the minister Luzzatti passed a law in favour of re-afforestation and the creation of a State domain of forests. In Germany there are 17,000,000 hectares of forest, of which 4,500,000 belong to the State; in Sweden, 20,000,000; in the United States, 200,000,000; and in Canada, 323,000,000 hectares.

place, and one litre then weighs 916·74 grms. For this reason ice formed in rivers and in the sea floats; if ice had not this important property all our lakes would consist of nothing but enormous masses of ice, and the earth would perhaps be uninhabitable by man.

If water is cooled in strong vessels, completely full and so closed that it cannot expand, it does not solidify even at very low temperatures (at − 24°, Boussingault).

At a pressure of 760 mm. ice always melts at 0° (fundamental temperature in thermometry, triple point, *see* p. 120).

Ice evaporates even below 0°. It is a bad conductor of heat and completely adiathermic for dark rays. It is electrified by friction, but does not conduct electricity. One kilo of ice at 0° absorbs 80 Cals. (more exactly 79·6 Cals., as fixed by the International Congress on Refrigeration, New York, 1913) in melting to 1 kilo of water at 0°. It crystallises in the hexagonal system, as may easily be seen by examining the crystals forming snowflakes.

Tammann (1909–1910) has shown that water contains molecules of at least two kinds corresponding with different forms of ice. Ice I, the ordinary stable hexagonal variety, consists solely of poly-molecules (which abound in water); ice II of an indefinite and less stable crystalline form; ice III, which separates crystalline from water under pressure (hence containing fewer polymerised molecules) is more stable, contains only mono-molecules, and is of unknown crystalline form; ice IV is less stable and more compact than ice I, and is formed by the spontaneous crystallisation of supercooled water obtained by slow cooling. When melted, ice IV is transformed immediately into ice I, with marked rise in pressure; it is probably tetragonal.

Pure water has neither smell nor taste, and is colourless in thin layers; in layers of more than 2 metres thickness it is slightly bluish in colour, but the colour varies with the dissolved or suspended substances. Its coefficient of compressibility is very small: 0·000,045 per atmosphere. The critical temperature of water is 365°. The velocity of transmission of pressure in water is equal to that of sound in the same medium.

Water is 773 times (or 819 times) as heavy as air at 0° (or 15°).

The conductivity for heat is small, but greater than that of all other liquids except mercury.

It has been noted already that water evaporates at all temperatures (vapour pressure, *see* p. 85), and the more rapidly the higher the temperature, the drier the air, and the less the pressure. In closed vessels a constant quantity evaporates at each temperature, and the vapour is thus at a definite pressure which increases or diminishes with the temperature. At 100° the vapour pressure of water is 760 mm. that is, it is equal to the normal atmospheric pressure, and therefore water boils at 100°; even at low temperatures water has a definite vapour pressure.[1] The temperature of ebullition of water

---

[1] VAPOUR PRESSURE OF WATER, ACCORDING TO REGNAULT, IN MM. OF MERCURY

t	mm.	*t*	mm.	*t*	mm.	*t*	mm.	*t*	atm.	*t*	atm.
−20°	0·916	16	13·536	26	24·988	60	148·791	130	2·6 at.	180	9·9 at.
− 5°	3·115	17	14·421	27	26·505	70	233·093	135	3·1 ,,	185	11·1 ,,
0°	4·525	18	15·357	28	28·101	80	354·643	140	3·6 ,,	190	12·4 ,,
+ 5°	6·471	19	16·346	29	29·782	90	525·692	145	4·1 ,,	195	13·8 ,,
10	9·165	20	17·391	30	31·548	100	760·(1 at.)	150	4·7 ,,	200	15·3 ,,
11	9·792	21	18·495	35	41·827	105	1·19 at.	155	5·4 ,,	205	17·0 ,,
12	10·457	22	19·659	40	54·906	110	1·41 ,,	160	6·1 ,,	210	18·8 ,,
13	11·162	23	20·888	45	71·391	115	1·67 ,,	165	6·9 ,,	215	21·0 ,,
14	11·908	24	22·184	50	91·982	120	1·94 ,,	170	7·8 ,,	220	22·9 ,,
15	12·699	25	23·550	55	117·478	125	2·29 ,,	175	8·8 ,,	230	25·5 ,,

These temperatures also show the boiling-points of water at the corresponding pressures.

alters with the pressure; in a vacuum of 90 mm. water boils at about 50°. When water evaporates without application of heat it abstracts the necessary heat from its surroundings. To maintain water as such, even above 100°, a pressure is required which alters with the temperature; the corresponding density of the steam increases as the temperature rises, and its heat of condensation also is variable.[1]

On evaporation water acquires a volume 1696 times greater than before. The ebullition of water is more regular the greater the quantity of dissolved air which it contains; it proceeds more regularly in metal vessels; in glass vessels with smooth walls water boils at about 101°, and even greater super-heating easily occurs, producing irregular ebullition (bumping). This super-heating can be avoided by placing a few fragments of glass or metal in the vessel.

On pouring water into vessels heated to more than 200° a thin layer of steam is formed, which is a bad conductor of heat, and insulates the water from the sides of the vessel, causing it to acquire the so-called *spheroidal state ;* on cooling the sides of the vessel below 171° the water comes in contact with them and is suddenly transformed into very large volumes of steam, which may cause the violent bursting of the vessel if this is closed; in this way the bursting of boilers which are badly supervised or are lined with heavy incrustations is explained.

---

[1] At 1 atmosphere 1 kilo of steam, in condensing to water at 0°, gives off 636 Cals., and at 16 atmospheres 670 Cals. When the pressure of the steam falls from 12 atmospheres to 0·12 atmosphere the volume increases from 1 to 100, but the steam does not lose much heat. The thermal equivalent of a horse-power-hour is $\frac{3600 \times 75}{426} = 600$ Cals., and since steam enters a steam-engine with about 660 Cals., the theoretical output of a steam-engine would be about 1 h.p.-hour per kilo of steam. In practice there are cases where 6 or even 16 kilos of steam are required per h.p.-hour, so that the efficiency is only 16·7 per cent. or even 6 per cent. of that theoretically expected, but it must be remembered that part of these calories are furnished by the condensation of the steam to water, so that, for example, when the 6 kilos of steam at 10 atmospheres escape from the engine at 1 atmosphere they have only given up 35 Cals. and are therefore not able to produce the horse-power, which requires 600 Cals., for this would require that part of the 6 kilos of steam should be condensed to water (as is usually the case !—*Translator*). In ordinary steam-engines the average consumption is 8 kilos of steam per h.p.-hour. Appreciable economy is effected by using superheated steam. Thus, when an engine is worked with saturated steam of the thermal capacity 652 Cals. per kilo, this leaves the engine at a pressure of 0·13 kilo with a thermal capacity of 547 Cals., so that 105 Cals. are utilised per kilo of steam. Steam superheated to the extent of 64° has a thermal capacity of 684 Cals. ($= 652 + 64 \times 0{\cdot}5$, 0·5 being the specific heat of steam) and leaves the engine at a pressure of 0·13 kilo and with a thermal capacity of 545 Cals., so that 139 Cals. are utilised per kilo of the superheated steam. In the former case, 10 kilos of steam per hour are required to generate 1 h.p., and in the latter only 7 kilos.

TEMPERATURE, DENSITY, AND HEAT OF CONDENSATION OF STEAM AT VARIOUS PRESSURES

Pressure in atmospheres	Temperature in degrees	Density of steam in kilogrms. per cubic metre	Heat of condensation in Calories, per kilo of steam, to water at same temperature	Pressure in atmospheres	Temperature in degrees	Density of steam in kilogrms. per cubic metre	Heat of condensation in Calories, per kilo of steam, to water at same temperature.
1·0	100°	0·606	536·0	3·25	136·6°	1·835	510·3
1·1	102·7°	0·663	534·3	3·50	139·2°	1·968	508·5
1·2	105·2°	0·719	532·5	3·75	141·6°	2·099	506·8
1·25	106·3°	0·747	531·7	4·00	144·0°	2·230	505·0
1·50	111·7°	0·887	527·9	4·25	146·2°	2·361	503·5
1·75	116·4°	1·023	524·6	4·50	148·3°	2·491	502·0
2·00	120·6°	1·163	521·6	4·75	150·3°	2·621	500·6
2·25	124·3°	1·299	519·0	5·00	151·2°	2·750	500·0
2·50	127·8°	1·434	516·5	5·25	154·0°	2·817	498·0
2·75	130·9°	1·569	514·3	5·50	155·8°	3·007	496·7
3·00	133·9°	1·702	512·2	5·75	157·5°	3·135	494·5

In order to transform 1 grm. of water at 0° into steam at 100° 636 cals. are required; to transform 1 grm. of water at 100° into steam at 100° 536 cals. are required, and this is called the *heat of evaporation.*[1]

Water dissolves some salts with absorption of heat, but with others (anhydrides), and with some acids, oxides, etc., heat is evolved on solution. The solubility of salts increases in general on heating, and is constant at any given temperature, so that the densities of saturated solutions at given temperatures are also constant. The freezing-point of saline solutions is lower than 0°, and the more so the greater the quantity of salt dissolved. For each molecule of anhydrous salt dissolved in 300 mols. of water, the freezing-point is lowered by 0·685° (Raoult, 1883).

The ice which separates from salt solutions is almost pure and only contains traces of salt which are mechanically enclosed. Thus, on freezing sea water the ice which separates only contains 1·58 grms. of chlorine per kilo, that is, about one-twentieth of the original quantity. In this way aqueous saline solutions can be concentrated, the ice being separated as it is formed. As far back as the Middle Ages the light wines of bad seasons were concentrated by freezing.

The boiling-points of aqueous saline solutions are higher than 100° and rise with the concentration. The saturated solutions have the highest boiling-points.[2]

A thermometer immersed in the vapours of a boiling saline solution always indicates 100°, although the vapour in the vicinity of the liquid may be hotter, and this occurs because pure water condenses on the bulb of the thermometer and boils at 100°. If the thermometer were previously heated to above 100° it would then indicate the true temperature of the vapour.[3]

The vapour pressures of saline solutions are lower than that of pure water by amounts directly proportional to the concentration.

The density of aqueous solutions of gases (*e. g.*, NH_3 and HCl) may be greater or smaller than that of pure water. On freezing such solutions the

---

[1] The *heat of evaporation* of a liquid comprises the work necessary to overcome the cohesion or mutual attraction of the molecules (internal work) and that necessary to overcome the external pressure (external work). The internal work is always much greater than the external work; thus, for water we have the following values when it is evaporated at various temperatures. We also add the heats of evaporation of some other substances.

—	Heat of evap.	Heat of ext. work	Heat of int. work	—	Heat of evap.	Heat of ext. work	Heat of int. work
	Cals.	Cals.	Cals.		Cals.	Cals.	Cals.
Water at 0°	607	31·1	575·9	Carbon tetrachloride at 0°	52	3·4	48·6
,, ,, 50°	571·6	35·5	536·1	,, disulphide at 0°	90	7·2	82·8
,, ,, 100°	536·2	40·2	496	Liq. sulphur dioxide	94·5	—	—
,, ,, 150°	500·8	44·1	456·7	,, ammonia	315	—	—
Ether at 0°	94	7·5	86·5	,, air	125	—	—
Alcohol at 0°	236·5	13·1	223·4	Methyl ether	130	—	—
Acetone	140·5	8·7	131·8	Carbon dioxide	84	—	—
Chloroform at 0°	67	4·5	62·5				

[2] By adding the following quantities of salts to 100 parts of water the following boiling-points are obtained:

Boiling-point	101°	102°	103°	104°	105°	106°	110°	115°	120°	130°	160°
Calcium chloride	10·0	16·5	21·6	25·8	29·4	32·6	44·0	58·6	73·6	104·6	212
Sodium ,,	7·7	13·4	18·3	23·1	27·7	31·8	—	—	—	—	—
,, nitrate	9·3	18·7	28·2	37·9	47·7	57·6	98·9	153·7	212·6	—	—

[3] *Translator's note.*—It is generally recognised that the true temperature of the vapour in these cases is 100°.

gas evaporates completely (when it does not form solid compounds, such as chlorine hydrate).

CHEMICAL PROPERTIES. The chemical composition of water was first discovered by Cavendish in 1781 by burning hydrogen in oxygen. The certain demonstration of its quantitative composition was, however, first given by Lavoisier in 1783; he succeeded in decomposing water by passing its vapour through a tube containing red-hot iron, which combined with the oxygen of the water, setting free the hydrogen, which was collected in a measured bell-jar. Until 1750 water was held to be a simple substance.

By burning hydrogen under a bell-jar filled with air the formation of water, which condenses on the walls, can be immediately observed, and the water can easily be collected. The heat of formation of liquid water from the elements $H_2 + O$ is 286·2 Kj. (68,400 cals.), or 58,800 cals. for water in the form of vapour.

In order to demonstrate the chemical composition of water it is made feebly acid and decomposed in a voltameter with two limbs; two volumes of hydrogen collect at the negative pole and one volume of oxygen at the positive pole.

It can also be shown that two volumes of hydrogen and one of oxygen combine to form two volumes of steam by introducing the mixture into a eudiometer surrounded by a mantle in which the vapour of a substance which boils above 100° circulates (*e. g.*, amyl alcohol, which boils at 132°). On passing an electric spark through the three volumes of gas ($2H_2 + O_2 =$ three volumes) two volumes of steam are formed.

The exact gravimetric control of the chemical composition of water was first undertaken by Berzelius and Dulong in 1820, by passing hydrogen over a given weight of red-hot copper oxide and then weighing both the resulting water and the partially reduced copper oxide; the results obtained did not agree very well on account of imperfections in the apparatus. In 1843 Dumas, in co-operation with Stas, started a series of very careful experiments, taking all possible precautions to arrive at exact results, employing large quantities of dry hydrogen and weighing much water, in order to reduce the errors to a minimum; the weights were corrected to vacuum, etc. The quantities of hydrogen forming the water were deduced indirectly by subtracting the weight of oxygen, found from the reduction in weight of the copper oxide, from the weight of water formed. From nineteen analyses Dumas obtained as a mean result the percentage composition 11·23 per cent. of H, and 88·77 per cent. of O, which is very near to the theoretical composition as calculated from the formula.[1]

The question of the true molecular magnitude of water has been much discussed during recent years, and the results obtained agree in attributing to water the double formula $2H_2O$ (dihydrol), ice being composed of trihydrol ($3H_2O$) and steam of monohydrol ($1H_2O$). Liquid water, however, contains trihydrol at temperatures near 0° and monohydrol in the neighbourhood of 100°. For ice the formula $6H_2O$ or $12H_2O$ has also been given (Duclaux, 1911).

Many salts contain considerable quantities of water of crystallisation, which is liberated on heating, *e. g.*, the alums with 12 mols. of water, and sodium carbonate with 10 mols. of water ($Na_2CO_3 + 10H_2O$), etc.

Dalton in 1840, and Joule and Playfair at a later date, found that when many of these salts are melted they occupy precisely the volume which the water of crystallisation alone would occupy in the form of ice; this applies to sodium carbonate among other salts. In the case of other salts, however, the volume which they occupy when melted is equal to the sum of the volumes of the anhydrous salt and of the water which they contain, in the state of ice.

Some salts, *e. g.*, crystallised calcium chloride, dissolve in water with absorption of heat; others, on the contrary, such as the same calcium chloride when fused (and free from water), dissolve in water with heat evolution, as they combine with a certain number of water molecules during solution.

Finally, in discussing the chemical properties of water we must refer to its great importance as a factor in almost all chemical reactions, either as solvent, as a cause of electrolytic dissociation on which the possibility of so many chemical reactions depends, or as a

---

[1] *Translator's note.*—It is generally understood that the ratios of the atomic weights of these two elements are calculated from experimental results on the composition of water, and therefore the latter cannot be checked by the formula.

catalytic substance in numerous reactions which do not take place except in presence of traces of moisture, as has been shown by Baker (1894–1900) by the most varied examples.

SURFACE (DRAINAGE) WATER. This is abundant in some localities. When the water of the subsoil is unable to descend into lower strata it stagnates in the ground and may even rise to the surface or above it. By a suitable system of pipes (drainage) it can be caused to flow into channels with advantage to the soil. This water is ordinarily polluted by all the organic matter and manure which is present on the land. From the analysis of such water the amount of fertilising materials which it is removing may be deduced.

RIVER WATER. Water derived from melting snow and ice contains about 50 mgrms. of dry solids per litre, these ordinarily consisting of Na_2CO_3, K_2CO_3, and organic substances which sometimes colour the water in various tints. River water contains less bicarbonate than that of springs because whilst flowing in contact with air it liberates CO_2 from the bicarbonates and deposits carbonates of Ca, Mg, and Fe, whilst spring water holds these salts in solution in the form of bicarbonates. Thus the water of rivers contains less mineral matter in solution in the lower reaches than near the source. It is then also poorer in organic substances, as these are oxidised or gradually reduced through the agency of bacteria, except in cases where the original composition of the water is altered by the influx of tributaries or the drainage of towns.

The temperature of river water varies greatly at various seasons and according to the flow of the water. With rise of temperature and slackening of the current (through the effect of dams) the amount of dissolved organic matter is increased, as the foam and rubbish more easily undergo putrefaction. River water always contains the gases O, N, and CO_2.

LAKE WATER. This is fresh when the lake continuously receives water and there is a continuous outflow, and salt when an outflow is lacking. Sometimes freshwater lakes have a composition the same as that of the inflowing rivers. Lakes constitute reservoirs which are of the greatest value in dry seasons.

SALT LAKES are closed basins into which saline springs flow, or they have a bottom formed of salt or are remnants of seas which have at some time been separated by a rise of the land level, such as the Caspian and Dead Seas, Sea of Aral, etc.

The composition of their waters varies greatly; thus those of the Caspian Sea and the Sea of Aral contain considerable quantities of $MgSO_4$ and $CaSO_4$ and only small quantities of $MgCl_2$; on the whole they are not very salt. The two small lakes which communicate with the Caspian Sea have a different composition and are more concentrated, because the evaporation is rapid and the inflow considerable, while there is no outflow; they contain scarcely any calcium sulphate because they are rich in other salts which throw this salt out of solution, while the amount of $MgCl_2$, which is very soluble, is continually increasing.

The lake with the most concentrated water is the Dead Sea (sp. gr. 1·194 to 1·212,) the water of which contains neither Li, Sr, Mn, iodides nor nitrates, but is a concentrated solution of NaCl, $MgCl_2$, and $CaCl_2$; it contains 22·7 per cent. of salts, which are composed of 28 per cent. NaCl, 47 per cent. $MgCl_2$, 15·8 per cent. $CaCl_2$. The Pacific Ocean contains only 3·4 per cent. of salts. In some lakes in Egypt and the Ararat district there is also Na_2CO_3, Na_2SO_4, and K_2CO_3. Some volcanic lakes contain free sulphuric acid, HCl, and boric acid.[1]

SEA WATER. This contains large quantities of NaCl, $MgSO_4$, $MgCl_2$, and $CaSO_4$; it has therefore a salty bitter taste. It contains traces only of potassium salts, $CaCO_3$, $MgCO_3$, phosphates, F, Ba, Sr, Mn, As, Cu, Pb, Ag, Li, S, and also minimal traces of all substances which form the earth's crust. It contains more bromine than iodine (there is 0·01 grm. of NaI per litre). The number of bacteria in sea water ordinarily diminishes in the deeper regions, and in certain localities is almost zero at depths greater than 200 metres, whilst in other places bacteria are found even at depths of thousands of metres. (The depth near New Pomerania in the south-western Pacific was measured in 1909 and found to be 9400 metres.)

---

[1] According to the analysis of Stutzer and Reich (1907) the water of the Dead Sea has the following composition: sp. gr. 1·1546 at 17·5°; 13·57 grms. per litre of KCl; 87·88 of NaCl; 23·84 of $CaCl_2$; 89·91 of $MgCl_2$; 3·68 of $MgBr_2$; 1·41 of $CaSO_4$; and a trace of iron. The total solids amounted to 220·2 grms. per litre. Further analyses by Friedmann (1912) show slight increases in all these figures, the total residue being 238 grms. per litre.

On the average sea water contains 3 to 4 per cent. of salts, or less where there are large affluents, as in the Baltic, the water of which contains only 0·7 to 2 per cent. of salts. It is less salt near the shores, and more so, on the other hand, at great depths.[1]

The water of the Mediterranean is more concentrated than that of the Atlantic Ocean because few rivers flow into it and evaporation by the hot winds which blow across from Africa is very strong. The Red Sea is still more concentrated, owing to the absence of feeders (*see* preceding Note). Sea water has a total hardness of 750° to 1000° (French degrees) and a temporary hardness (French) of 44° to 70° (*see* Hardness *below*); we need not discuss the hardness of the Dead Sea, as it is of very little importance.

Sea water has a strong corrosive action on metals, copper being the most resistant of the common metals, especially if it contains five parts per thousand of arsenic. The resistance of iron is increased if it contains phosphorus or nickel and still better if it is coated with zinc (" galvanised ").

PROVISION OF POTABLE WATER FOR COMMUNITIES

The nations of antiquity had only water from springs or from cisterns in which rain water was collected; dug-out wells, constructed of masonry, were first devised by the Egyptians and then perfected by the Jews, who exercised much care in their construction. The Greeks, who had only used cisterns and springs, imported the use of wells from the East. The Romans at first used tanks and the bad water of the Tiber, but as their power progressed the necessity arose of satisfying more efficiently the growing needs of the community, and the supply of water was recognised as a question of State; covered aqueducts of stone were then constructed which carried the water from distances as far as thirty hours' journey.[2]

In some countries, such as Germany, France, and England, the use of spring water, which is abundant in those countries, was continued for some time, but other nations followed the example of Rome and constructed conduits of good water, recognising the disadvantages of tanks and wells, which became polluted and foul. Gradually, as communities collected into large centres and in towns closed in by walls and fortifications and subdivided by narrow streets, wells were excavated for drinking water in the narrow yard of each house, in the vicinity of stables, latrines, and refuse heaps. Things remained in this condition until our own times. Only now is the utility of pure water mains and of aqueducts being realised. In many towns, and especially in the country, sad to say, there is still no potable water, in spite of the fact that it has been shown that many infectious diseases are caused by bad water and claim many victims every year in the towns, and especially in the country. (*Translator's note.*—These remarks must be taken to apply more especially to Italian conditions.)

The Chinese of antiquity already recognised the hygienic importance of pure and abundant water, and even during their early civilisation they knew how to bore into the ground and obtain good water from the subsoil, and possessed such wells, now called artesian wells in Europe, by thousands. To-day in the province of U-thung-khiao alone,

---

[1] Recent analyses (1906) showed the following composition per litre: I. is from the Mediterranean near Tunis; II. from the Atlantic near Dieppe; and III. from the Red Sea.

	Density at 20°	$CaCO_3$	Acids: H_2SO_4	Cl	Br	Bases: CaO	MgO	Na_2O	K_2O	Total
I.	1·0287	0·126	2·516	21·676	0·072	0·617	2·365	15·584	0·510	38·97
II.	1·0239	0·099	2·120	17·830	0·060	0·519	1·993	13·410	0·413	32·42
III.	1·0270 at 10°	—	2·100	20·900	—	0·680	2·000	16·000	—	36·70

[2] Of the fourteen aqueducts constructed by the Romans the following are the most important:

Appia	(312 B.C.),	66½	kilos. long,	carrying	65,000	cu. metres of	spring	water daily.
Aniente Vetera	(272 ,,),	64	,,	,,	268,000	,,	river	,,
Marcia	(143 ,,),	91½	,,	,,	101,000	,,	spring	,,
Giulia, Vergine, Alsictina, carrying together					135,000	,,	,,	,,
Claudia	(A.D. 52),	69	kilos. long,	carrying	101,000	,,	,,	,,

Of the ancient Roman aqueducts only four remain to-day (Marcia, Vergine, Felice, and Paola), which furnish a good third of the supply of potable water of modern Rome. At the time of Julius Cæsar there were in Rome no fewer than 970 public baths, which consumed 700,000 cu. metres of water daily. The thermal springs of Diocletian and of Caracalla were world-famous, and their vestiges remain to-day. All over Germany, France, and Spain there are ruins of large aqueducts and celebrated thermal wells constructed by the ancient Romans.

in an area of 1000 sq. kilos. there are over 10,000 of these wells, and some of them are 900 metres deep with a diameter of 10 to 15 cms. These wells were known to the Egyptians, but at a much later date, and the first artesian wells in Europe were constructed in the county of Artois as late as about A.D. 1000, being named after the locality. In 1600 to 1700 artesian wells were also introduced into Italy, Germany, and England, and since those times their number has continually increased up to the present time.

TANKS. These serve to collect rain water in countries where springs are rare, especially in hot countries. They are excavated in the ground or rock, so that the water may remain fresh, and are lined with masonry or cement. Rain water, however, finally undergoes putrefaction, on account of the impurities collected and carried down from the atmosphere, so that it should be filtered before use. The tanks of Venice have at the bottom a layer of sand, which serves as a filter. There are large and fine tanks at Constantinople, Alexandria, etc. There were 1430 public tanks in Italy in 1903, of which only 398 gave potable water.

WELLS. Ordinary wells are excavated down to the first water-level of the subsoil, and their sides are clad with masonry. These are old-fashioned wells, open above and ready to receive any impurity whatever; the water is almost always polluted and is withdrawn in more or less dirty buckets mounted on a cord passing over a pulley; whenever rain is abundant they become turbid and to them typhoid infection is very largely due. In 1903 7000 of these existed in Italy for public use, distributed in 2700 communes. Instead of excavating wide and deep wells in masonry one may excavate a shallower well and then drive in at the centre an iron tube of a few centimetres diameter in order to arrive at a level where the subsoil water is deeper and purer. The lower end of the tube is perforated and protected by a grating which keeps out sand. A narrower tube dips into the first tube and is connected with a pump by which the water is drawn up. These wells are called American or Norton wells, from the name of the English engineer who first constructed them.

If iron tubes are sunk, by means of drilling, to greater depths, deposits of water are sometimes struck in the subsoil contained between two impermeable strata and coming from higher regions. When the upper impermeable layer is perforated the water often issues under pressure and may rise to the surface in the form of a fountain. If it does not rise to the surface it is pumped into reservoirs, whence it is distributed to the fountains and dwelling-houses. These wells are called artesian wells (*see above*). The artesian well of Grenelle at Paris is 647 metres deep, took seven years to drill (1833–1840), and supplies three million litres of pure water daily at a temperature of 37·7°. On the Place Hébert in Paris there is an artesian well, finished in 1888, 719 metres deep, which supplies water at 34·5°, has a mouth one metre wide, required twenty-two years to sink, and cost £100,000. The well at Mondorf, in Luxembourg, is 730 metres deep. At St. Louis,U.S.A., there was a very deep well which yielded rather sulphurous water, and in 1865 it was decided to deepen it in the hope of obtaining a purer supply; when a depth of 1200 metres was reached the granitic rock of the primitive formation was met with, and it was thus found impossible to obtain from the deeper well water of other character than before. The water of artesian wells is characterised by the absence of nitrates, and by the presence of only traces of sulphates and of organic matter; when it traverses peat, it contains also traces of ammonia. On the other hand, it contains much sodium as carbonate and chloride and does not contain oxygen if it has not been in contact with the atmosphere, because this is absorbed by the ferrous or manganous compounds and organic substances of the strata through which it passes.

The deeper the well the warmer the water; below the first 30 metres the temperature increases by about one degree for every 20 to 30 metres of depth. However, tanks and ordinary excavated wells satisfy modern hygienic requirements only very exceptionally, whilst artesian wells (drilled) often provide potable water. The firm of Piana of Badia Polesine alone constructed 5233 artesian wells up to 1901.

POTABLE WATER. This is water which passes all requirements necessary for human consumption. These requirements are enumerated below. For twenty-five years medical men have debated the question whether impure water is an important factor in spreading infectious diseases, such as cholera, typhoid, dysentery, etc.

Most German and English doctors have decided in the affirmative, and of late years a large proportion of the doctors of all nations have come to share this opinion.[1]

It is difficult to detect the specific bacteria, as it is not easy to distinguish them from the innumerable perfectly harmless species found even in good waters. Their presence is therefore demonstrated indirectly by the determination of certain characteristic substances which are derived from the bacterial decomposition of animal residues or dejecta, and which filter along with pathogenic bacteria into the water of wells, etc. Thus, chemical analysis also serves to establish if a water is infected or liable to infection.

Potable water should be colourless, odourless, limpid, not too cold in winter nor too hot in summer, of a temperature of 10° to 14°. It should be carried in iron and not in galvanised iron or leaden pipes, since these are easily attacked in presence of carbon dioxide and air.

All town and village well water contains, in larger or smaller quantity, the waste products of the animal organism. During infiltration through the soil these are transformed into numerous compounds which have not yet been well studied, and after a certain time in contact with air, produce mainly carbon dioxide, ammonia, nitrites, nitrates, and chlorides. The phosphates, potassium salts, organic nitrogen compounds, and ammonia are retained by the soil, whilst the chlorides, sulphates, and nitrates find their way into the wells or springs. When, however, the soil is no longer absorbent or is saturated, or only slightly aerated, ammonia and the intermediate decomposition products of the nitrogenous organic matter also find their way into the water. Thus not more than a minimal amount of chlorides and nitrates should be present in potable water; there should be no nitrites or ammonia, and exceedingly little organic matter (*see below*, Water Analysis).

The economic requirements of the modern State render necessary the supply of good and abundant water to the population. At the International Congress of Brussels in 1896 there was indicated as a minimal limit for towns of moderate importance the supply of 150 litres of potable water for each inhabitant per twenty-four hours; for large towns with more than 200,000 inhabitants 100 litres would suffice. In Germany the mean supply is 150 litres, in England 200 litres, in France 250 litres, and in America 500 litres. In Milan the mean consumption per inhabitant has increased rapidly of late years and has now risen to 140 litres. In Berlin, with more than 3,000,000 inhabitants, 136 million cu. metres of water were consumed in 1912, this being about 125 litres per head per day.

The water of common wells is not ordinarily potable because it is very easily polluted, and therefore the supply of good water to the people to-day constitutes one of the most important problems of social economy, the solution of which should not be left in the power of private citizens, more or less ignorant, or in that of speculators, more or less dishonest, but should be attended to by the collective social community.

---

[1] The mortality through typhoid in Milan in 1880 was 10 per 10,000 inhabitants; gradually, as drainage and good water were introduced, the mortality from typhoid diminished, and in the quinquennium 1901–1905 the average mortality from this cause was 3 per 10,000, that is, 180 deaths per annum, whilst if the conditions had been as in 1880 the number of deaths would have been 600. At Frankfort the mean annual mortality from typhoid from 1854 to 1875 was 6·2 per 10,000 inhabitants, whilst from 1876 to 1879—that is, after the introduction of a drainage system and drinking-water supply—it decreased to 2 per 10,000. In Hamburg the mean total mortality from 1845 to 1855 was 500 per 10,000 inhabitants, whilst after the drainage works, drinking-water supply, combustion of town rubbish, and sewage works were completed, the total mortality decreased to 220 per 10,000 per annum; that is to say, whilst Hamburg has 13,000 deaths per year, the number would have risen to 30,000 under the hygienic conditions of the past. In the United States there are 400,000 typhoid cases per annum with 35,000 deaths, that is, 12 per cent., whilst in Norway, Sweden, Germany, and Switzerland the percentage of deaths from typhoid is only 6 to 8 per cent.

The distribution of water should not take place through leaden pipes for reasons which will be explained below, but through pipes of cement or, better still, of cast- or wrought-iron.

Abundant water for the people and not only for those in the towns but also for the countryside, may be obtained in the following ways :

FROM RIVERS AND LAKES. When these are clean their water may sometimes serve for the supply of towns, but should always be filtered, as it contains many substances in suspension : clay, lime, eggs of insects and of worms, animal and vegetable remains, fibres, hair, etc. (*see below*, Filtration).

It is not desirable to leave this filtration to the consumers, as it will then be less careful and more costly; the filtration should be carried out at the central distributing station. Bacteria are only partially removed by filtration. The water of rivers is often too cold in winter and too warm in summer. Works for obtaining potable water from rivers are established at Lyons, Zurich, Trieste, etc., where it is purified by filtration.

WATER FROM THE SUBSOIL. Water from the first water horizon, which is often found a few metres below the surface, can sometimes be used if taken from localities far from inhabited places. It does not matter if there are cultivated fields above, as the harmful substances and the greater portion of those which are soluble are retained by the soil, if the water horizon is sufficiently deep.

The water may be pure and its temperature more constant than that of river water. It is collected in channels and then in wells, from which it is raised by pumping to high reservoirs and thence distributed to the inhabitants.

The water of the subsoil which flows between two layers of impermeable clay is usually much purer and proceeds from higher levels. This water is raised by artesian wells (*see above*) and costs relatively little : from 0·2*d.* to 0·5*d.* per cubic metre.[1]

---

[1] In Milan the problem of potable water has been solved since 1889 by taking water from the subsoil at depths of 30 to 80 metres by means of wells excavated by the Canadian method, one at least each year, and there are now about forty wells which supply 25,000,000 cu. metres of water per annum, one-third of which is destined for the public service (street watering, fountains, urinals, public buildings, schools, markets, etc.). Whilst in 1889 only 4300 cu. metres were consumed for domestic purposes, in 1895 this figure had risen to 500,000, and in 1900 to more than 3,000,000 cu. metres, whilst to-day the distribution of potable water in Milan is shown by the following figures :

USE		1915	1914	1910	1909	1908	1907
Private	cu. metres	25,600,000	23,500,000	16,060,000	14,771,580	13,023,860	11,070,781
Works	,,	6,600,000	5,280,000	3,656,000	3,747,587	3,261,344	2,633,288
Public roads	,,	8,150,000	7,815,000	7,147,000	6,335,920	5,747,486	5,296,000
Total	,,	40,350,000	36,595,000	26,863,000	24,855,087	22,032,690	19,000,069

Milan to-day has a supply of more than 7000 litres per second, that is, 640,000 cu. metres per twenty-four hours. The cast-iron tubes of the wells are of 0·80 metre diameter, and the wells cost about £12 16*s.* per metre. Each well when finished, including all implements, etc., costs from £480 to £600, which is not inclusive of the installation of buildings and machinery (pumps, boilers, motors, etc.) attached to each group of wells (each installation costs from £4400 to £6000). The water is collected in two large reservoirs at the top of the two towers of Castello Sforzesco. The first was of iron, of the Intze type, and was constructed in 1893, with a capacity of 1200 cu. metres; the second, of 1500 cu. metres capacity, was constructed in 1904, in reinforced concrete, of cylindrical shape, with a flat base. The potable water-mains of Milan have to-day reached a length of 230 kilometres (145 miles) and supply water to about 7500 houses, which pay from 1·44*d.* to 1·92*d.* per cu. metre (4·2*d.* to 5·4*d.* per 100 cu. ft.). After 1912 the charges were lowered.

The mean temperature of the drinking water of Milan is 13°, or 15° in the mains; the composition per litre of the water from the different wells in 1905 was as follows :

	Grms.		Grms.
Total residue at 150° . . .	0·145 –0·250	Lime (as CaO)	0·0500–0·0800
Loss on ignition	0·0400–0·0550	Magnesia (as MgO) . .	0·0130–0·0210
Organic matter (as oxygen) .	0·0004–0·0007	Soda (as Na_2O)	0·0070–0·0100
Sulphates (as SO_2) . . .	0·0040–0·0170	Iron	trace–0·0010
Nitrates (as N_2O_5) . . .	0·0009–0·0036	Ammonia	zero
Silicates (as SiO_2)	0·0150–0·0180	Total hardness	9°–17° (French)
Chlorides (as Cl)	0·0054–0·0092	Permanent hardness . .	3°–5° (,,)

The subsoil water of Milan shows a dry residue of 0·500 grm. per litre at a depth of 4 metres, whilst at a depth of 18 metres there is only 0·220 grm. of dry residue per litre, and the amounts of nitrates and chlorides diminish in the same proportion.

AQUEDUCTS. When good water is not to be obtained from rivers or from the subsoil it is necessary to transport it from more or less distant lakes or natural springs, which yield fresh pure water, rich in carbon dioxide, but before starting works of so costly a character it is necessary to study all the hydrological factors of the locality over a series of years in order to be certain of the yield and continuity of the springs during the different seasons of the year. It is not to be denied that when the springs are fed by glaciers or by snow they flow abundantly only in spring and summer. It is also necessary carefully to control the materials of construction and to exercise a vigilant supervision to prevent infiltration.

For potable water in general, but especially for water rich in dissolved CO_2 and air, it is necessary to avoid leaden pipes. Lead is dissolved most readily by aerated water, and in proportion to the amount of oxygen present, while the action also depends on whether the water flows rapidly or remains stagnant in the pipes. Free carbon dioxide also facilitates solution of lead, though to a less extent than oxygen, whilst carbonates, on the other hand, are harmless. It is necessary to prevent replacement of the water in the pipes by air. In order to avoid all danger the use of leaden pipes for the transmission of potable water should be prohibited.

For large mains pipes of cement, or better of cast-iron, are used, and for small mains wrought-iron tubes. Galvanised (zinc-lined) iron tubes contaminate the water with zinc. Water which is not very hard and is rich in CO_2 and bicarbonates and also much aerated attacks even iron pipes; in such cases pipes of tinned iron are used, as is now done in some towns abroad (*i. e.*, outside Italy) when iron and leaden pipes are rapidly corroded. In Germany glass tubes are used in certain cases.

The presence of organic matter greatly increases the corrosion of leaden and iron tubes.

Potable water supplied by aqueducts is generally dearer than that from artesian wells. In a project to supply water to the city of Cremona, with a conduit 40 kilometres long (twenty-five miles) and at an expense of about £80,000, the water would have cost 1·5*d.* per cu. metre, whilst by obtaining it from the subsoil it costs less than 0·4*d.*

The Apulian Aqueduct will cost £5,000,000, and will furnish potable water to 228 cities and boroughs (over 2,000,000 inhabitants) at the rate of 60 to 200 litres per inhabitant per twenty-four hours.[1]

In order to supply the 300,000 inhabitants of Los Angeles, California, with potable

[1] For twenty-five years the southern population of Italy have persistently demanded the construction of the Apulian aqueduct, which would have regenerated the life of that beautiful but neglected region.

Finally, in 1898, the Government approved of a law which arranged for the consideration of a definite project for conducting and distributing water from the Sele in Apulia. The laws of June 26, 1902, and July 8, 1904, declared it to be a work of public utility and claiming the attention of the State. A *consorzio* (partnership) was then established between the State and the provinces of Foggia, Bari, and Lecce, and the respective councils were invited to nominate their representatives on the Board of Administration.

The concessionaire was to complete the construction of the aqueduct by 1920 and was then to work it and maintain it for ninety years, after which it passed freely into the ownership of the consorzio, who were then to be responsible for its working and maintenance. The State contributed £4,000,000 to the cost and the provinces £1,000,000.

In an international competition the most advantageous offer was made by the Societa Ercole Antico e Soci, and the concession was awarded to them after they had deposited the necessary guarantee of £240,000.

The large masonry channel into which the springs will be diverted, after passing through a first tunnel of about 400 metres, will pierce the Apennines by a tunnel which will be 15 kilos. (9 miles) long and will then discharge into the Ficocchia torrent, an affluent of the Ofanto River. In this way the water of the Sele springs, which actually form part of the drainage system of the Tyrrhenian Sea, will be diverted into one of the affluents of the Adriatic.

The grand canal, of navigable dimensions, will be constructed of masonry, will pass along a portion of the Ofanto Valley, turn to the east at the base of Monte Vulture, with a stretch, generally in galleries, as far as the neighbourhood of Venosa, where the large branch for the province of Foggia will start; it will then proceed past the Palace of San Gervasio and Spinazzola, meeting the mountainous chain of the Murge, which it will follow to its extremity at the boundary of the provinces of Bari and Lecce. This canal will be 236 kilos. (148 miles) long. To it will be attached the numerous branches which will distribute the water to the three Apulian provinces, which will together be 1600 kilos. (1000 miles) long, and to which it will be necessary to add 800 kilos. (500 miles) of pipe-lines for the urban distributing systems. It will also be necessary to construct 146 reservoirs of a joint capacity of about 263,661 cu. metres.

water an aqueduct has been constructed of reinforced cement, 386 kilos. long (241 miles), 4·58 metres wide, and 2·75 metres deep, costing £4,600,000, which takes water from the Owens River; it serves to irrigate a stretch of 400 kilos. (250 miles) of country and furnishes 120,000 h.p. The City of New York has the Croton aqueduct and is constructing another which will cost more than £40,000,000, and will deliver two million cu. metres of water daily, and thus the mean supply of water per head of the population will rise from 125 to 500 litres per day (500 litres = 114 gals.).

In 1893 the City of Paris disposed of 710,000 cu. metres of potable water, of which 290,000 cu. metres were obtained from various springs by means of aqueducts, of which the most notable is that from Havre, 102 kilos. (64 miles) long and of 1·5 metres diameter. In 1906 900,000 cu. metres per day of potable water were available at Paris. The daily stock in the various reservoirs was 500,000 cu. metres in 1900.

WATER ANALYSIS. In order to decide if a water is potable it is sometimes necessary to make a bacteriological examination, which should be conducted by a specialist, as well as a chemical analysis. The sample of water for this examination should be collected directly in sterilised bottles on the spot; these bottles must be immediately placed in an ice chest and sent to the bacteriologist, in order to avoid multiplication of the bacteria.

The samples for the chemical analysis should be collected in clean glass bottles, if possible with glass stoppers. In the greater number of cases chemical analysis of the water will show whether it is potable, and also whether it is suitable for various industries (*see below*). In order that a water should be potable the dissolved substances should not exceed the following limits: Per litre of water: Dry residue 0·300 grm.; organic matter (expressed as oxygen) 0·0025 grm., or expressed as permanganate 0·01 grm.; lime and magnesia ($CaO + MgO$) 0·200 grm.; sulphuric acid as sulphates (expressed as SO_3) 0·100 grm.; nitric acid (as N_2O_5) 0·012 grm.; chlorine (Cl) 0·030 grm.; ammonia, zero or not more than 0·0002 grm. of albuminoid ammonia; nitrites, zero. (Prescription of the municipal laboratory of Milan.)[1]

---

[1] We here give very shortly the methods of water analysis.

The *dry residue* is determined by evaporating 300–350 c.c. on the water-bath in a tared platinum dish, then drying in an oven at 170° and weighing the residue. By heating to redness and reweighing, the *residue on calcination is obtained*, the organic matter being burnt.

The dry residue of a potable water should show practically no blackening or volatility on incineration, as this would indicate an excessive amount of organic matter.

The *lime, magnesia*, and *iron*, which are present in the water as bicarbonates, and the alumina and silica, are determined in the dry residue from at least 1 litre of water; the residue is dissolved in HCl and the silica separated on a tared filter; in the filtrate the iron and alumina are precipitated with ammonia, filtered, dried, and weighed; in the second filtrate the lime is precipitated with ammonium oxalate and filtered; in the third filtrate the magnesia is precipitated with sodium phosphate. All these substances are expressed in the results as oxides: CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2 (or as metallic cations: Ca, Mg, Al, Fe).

The *chlorides* are determined by titrating 100 c.c. of the water with $\frac{N}{10}$ silver nitrate solution, employing as indicator one drop of a concentrated solution of potassium chromate, which becomes red when all the chloride has been precipitated as white AgCl. The results are expressed as chlorine (Cl).

With industrial waters special interest attaches to the determination of the magnesium chloride. Pfeiffer's method (1909), based on the volatility of the chlorine of magnesium chloride when the dry residue is heated, is inexact owing to the influence of $CaSO_4$, NaCl, and $MgSO_4$, which are always present. Good results are, however, obtained by Bosshard and Burawzow's method (1913): the dry residue of a given volume of water is treated with a mixture of equal volumes of alcohol and ether, this dissolving only the magnesium and calcium chlorides. The solvent is then expelled and in the residue the total chlorine is determined by means of silver nitrate and the calcium as oxalate, the magnesium being calculated by difference. The presence of gypsum and calcium bicarbonate has no influence on the determination of the magnesium.

Nitrates are detected qualitatively by the blue coloration formed on adding a crystal of diphenylamine and 2 c.c. of strong sulphuric acid to 1 c.c. of the water; they are determined quantitatively by the Schlösing-Schulze-Tiemann method by evaporating 100 c.c. of the water to 10 c.c., decomposing with ferrous chloride and acid in a suitable apparatus, and measuring

PURIFICATION OF WATER FOR ALIMENTARY PURPOSES. The use of chemical reagents is generally inadvisable, and is applied only in exceptional cases to diminish the hardness, as is explained below for industrial purposes, where the methods of diminishing the amounts of organic matter and eliminating iron are also explained.

To obtain potable water from suspected or impure water, one has recourse to filtration or sterilisation.

FILTRATION. In order to eliminate suspended matter (and in part also the bacteria) and in some slight degree to decompose any dissolved substances, the following materials have been proposed: wool, sponge, felt, porous soil, blast-furnace slag, asbestos, bone charcoal, briquetted charcoal (consisting of a mixture of wood charcoal, bone charcoal, sawdust, and tar or asphalt, all compressed in a mould and then gently roasted). Organic materials, such as wood, felt, sponge, etc., are, however, to be condemned as they assist the putrefaction of the water. Excepting the filters with a carbon basis they all have a minimal absorbent capacity for the suspended matter, and filters which have little absorptive power end by making the water worse than before. As the filters are but little aerated only a minimal chemical decomposition of the dissolved matter takes place.

The large filters for towns consist exclusively of layers of sand, more or less fine; the more finely divided the suspended matter in the water is, the less water will pass in a given time through the same filtering materials of a given thickness and area. If, for example, 3 to 5 cu. metres of Thames water will pass through 1 sq. metre of a filtering medium in twenty-four hours, only 1·7 cu. metres of Elbe water will pass through in the same time, as the suspended matter in the latter is much the finer. Large filters are formed of large tanks of masonry or iron; the water enters below, first passes through layers composed of gravel and clay, then through coarse quartz, and finally through fine sand with grains of 0·5 to 1 mm. diameter. The complete bed may be 60 cms. deep, and each single layer about 15 cms.

The bacteria are not at first retained, but when the pores of the filter bed are partially closed by mud from the water the number of bacteria diminishes considerably. For example, at Zürich the lake water contains 50 to 2000 bacteria per c.c. before filtration; after filtration it contains only 1 to 30 bacteria per c.c. The upper layer of fine sand is changed the more frequently as it easily becomes clogged.

In America these filters are improved by mixing aluminium sulphate with the sand. At Pittsburg, filtration of the water resulted in the diminution of the number of deaths by 400 per annum.

For small domestic use various convenient filters are sold in which the water passes, with good results, through compact but porous stone blocks analogous to the Chamberland filters. Malfitano has proposed filtration through semipermeable colloidal membranes, which would give the very best results from the bacteriological standpoint.

---

the nitric oxide evolved. The results are expressed as nitric anhydride (N_2O_5); 1 c.c. of NO at 0° and 760 mm. corresponds with 2·417 mgrms. of N_2O_5.

Nitrites are quickly detected qualitatively by adding to 50 c.c. of water 2 c.c. of starch paste and zinc iodide and 1 c.c. of dilute sulphuric acid (1 : 3), when a blue coloration is shown in a few minutes if they are present; or 1 c.c. of sulphuric acid and 1 c.c. of metaphenylenediamine sulphate solution may be added, these giving a red coloration.

Sulphates are precipitated by barium chloride, and the results expressed as SO_3.

Ammonia is tested for qualitatively only, with Nessler's reagent (*see* Mercuric Iodide), after separation of the lime, magnesia, etc., by means of sodium carbonate. A mere yellow coloration shows the presence of ammonia, whilst a precipitate indicates a large amount.

Carbon dioxide, combined and half combined (CO_2), is precipitated by a measured excess of standard lime-water, and the excess then titrated back with a standard solution of oxalic acid.

The organic matter is determined with $\frac{N}{100}$ solution of potassium permanganate which is first titrated with $\frac{N}{100}$ oxalic acid solution; the permanganate solution is added to 100 c.c. of the boiling water acidified with sulphuric acid. By multiplying the number of c.c. of permanganate used by 0·00316 the organic matter is expressed in terms of permanganate, whilst by multiplying by 0·0008 it is expressed as oxygen required per litre of water. It is estimated that one part of permanganate oxidises about five parts of organic matter.

STERILISATION OF WATER. In order to sterilise water, that is, to kill all the pathogenic germs and diminish the organic matter, Schenilowa proposed in 1898 to add a solution of potassium permanganate and then filter through charcoal. This method is not always certain, even if calcium permanganate is used together with the electric current. In the same way the effects of adding small quantities of bromine as proposed by Schumburg in 1899, or of 5 grms. of chloride of lime per cu. metre proposed by Traube in 1892 and Lode in 1900 (although Mason still insisted on its efficiency in 1909), are not certain, as has been clearly shown by Schüder, by Engels (1902), and by Hetsch (1906); the last has found that the ferric chloride method of Duyk is useless (mixture of ferric chloride and sodium or calcium hypochlorite) and that the silver fluoride (tachyol) of Paterno and Cingolani (1903), and the silver fluosilicate (isotachyol) of Paterno are not always effective; Foa and Corsini (1904) came to the same conclusion with regard to tachyol. In the United States, some 400 villages and towns make use of chlorine (hypochlorite) to sterilise the water (1 kilo per 350 cu. metres), with satisfactory results.[1]

G. T. Moore in America (1905) uses 1 grm. of copper sulphate per hectolitre of water, but the soundness of this method is still contested, whilst more satisfactory results, though they are not yet definite, have been obtained with hydrogen peroxide.

Sterilisation by boiling has the disadvantage that all the spores of the pathogenic organisms are not killed, and that the gases and bicarbonate dissolved in the water are lost, thus altering its taste and digestibility. Heating under pressure at 110° (Vaillard's system) is preferable, but is not always economical and is not adaptable to large-scale production.

Of all methods of sterilisation proposed up to the present the safest and most economical is the treatment of the water with ozone. In 1891 Ohmüller first investigated the behaviour of the various species of bacteria in presence of slightly ozonised air, and succeeded in showing that none of the pathogenic bacteria, especially when distributed in water, resisted the action of ozone, even when much diluted. *Bacterium subtilis* (hay bacillus) alone resists the action of ozone (and also a temperature of 110°), but it is a perfectly inoffensive organism both for man and for animals.

Hence the solution of the great problem of the sterilisation of water only awaited the time when it would be possible to obtain ozone cheaply and in large quantity (*see* Ozone, p. 203).

To-day the solution of the problem is an accomplished fact, and there are in Europe many important plants for the ozonisation of water (in 1913 there were thirty, three of them being in Germany).

In 1900 the firm of Siemens and Halske erected the first plant in their own works at Martinickenfeld, near Berlin, employing water from the Spree contaminated with Berlin sewage. Ten cubic metres were purified per hour with a current at 15,000 volts. The water passed first through the tube *D* into an upper reservoir and then through the tube

---

[1] In spite of criticism, the method of sterilising water by means of calcium hypochlorite has spread in various countries, including Germany, where the original opposition to it has been overcome. It is a simple and economical process, but requires rigorous control, since the strength of commercial chloride of lime varies greatly (15–38 per cent. of available chlorine), and since thorough mixing is required as well as the lapse of a certain time for the chlorine to act (10–12 hours). When the water is deficient in limpidity, it should be filtered.

The amount of the reagent to be added varies with the quality of the water (if iron or organic matter is present the method is not used) and with the strength of the hypochlorite; 0·5 gram of a good product usually suffices for 1 cu. metre of the water, and as much as 1 gram is seldom used. Two reservoirs are necessary, each capable of holding a 24 hours' supply of water. The requisite amount of the hypochlorite is mixed thoroughly and for some time with the water, and the latter then left for 15–20 hours with one mixing during this time. Any excess of chlorine, which imparts a phenolic flavour to the water, is then eliminated by addition of a quantity of sodium thiosulphate (improperly termed hyposulphite) corresponding with about one-half of the hypochlorite used; after thorough mixing, the water is left for 1–2 hours and is then ready for use. This addition costs less than 0·1*d*. per cu. metre, and may often be used with advantage when the employment of ozone or ultra-violet rays is impossible (*see later*).

C into a rapid Krönhke filter in order to remove suspended matter (Fig. 78). It was then pumped into another reservoir over a tower lined internally with cement and filled with pebbles below and sand above. A current of ozonised air entered at the base of this tower, whilst the water fell from above as a fine spray, meeting the current of ozone. The ozonised air was produced by the passage of previously dried air through an ozoniser. The water was collected at the base of the tower in reservoirs, and a few minutes afterwards it no longer gave any reaction for ozone and was sterilised. The Spree water contained 200,000 and sometimes 600,000 bacteria per c.c. The ozone attacked first the dissolved organic matter and then the bacteria.

The sterilisation was always satisfactory and the results were checked by Ohmüller of the Imperial Bureau of Hygiene in Berlin, by Proskauer and by Schüder of the Koch Institute. The quantity of ozone required varies with the nature of the water, being the greater the more organic matter there is present in the water; generally at least 1 cu. metre of ozonised air, containing 8 to 9 grms. of ozone, is required for each cubic metre of water; the water which has just passed through the ozonising tower should still show a strong reaction for ozone with potassium iodide-starch test papers.

Artificial cultures of the microbes of cholera and typhoid were also passed through the plant in order to ascertain whether they could be detected by careful special cultures in the water which had been treated.

In every case the water proved to be absolutely free from pathogenic organisms and only very few common microbes remained, such as are found in the purest spring water. After the action of ozone the water does not ordinarily contain more than five to ten microbes per c.c., and often none at all are shown by the gelatine cultures even on the third day.

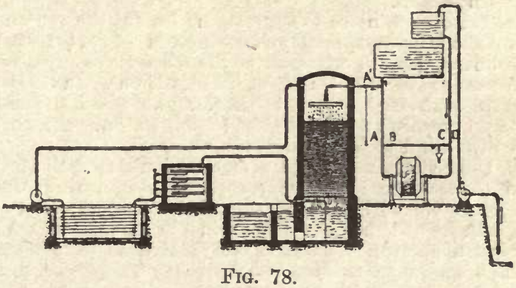


Fig. 78.

After these satisfactory results the firm of Siemens and Halske erected a much larger plant at Wiesbaden in 1902, for a maximum production of 250 cu. metres of potable water per hour.

Shortly afterwards the same firm erected another plant, providing 60 cu. metres of water per hour, for the supply of all the drinking water of the Prussian city of Paderborn, with 50,000 inhabitants. Since that time Paderborn has been free from the typhoid epidemics which had previously occurred every year. The cost of sterilising water at Wiesbaden, including all expenses, amortisation, and interest for the complete plant, is less than 0·3*d.* per cu. metre (0·01*d.* per cu. ft.). In the Russo-Japanese War the Russians successfully used water-ozonising plants mounted on small carts.

At Nice the ozonisation of the water was commenced with Otto's apparatus in 1906 (120 cu. metres of water per hour). At Philadelphia a large plant for the ozonisation of water has also been erected (1905) and other plants have been recently constructed in some French towns. In Italy an experimental plant has been erected at Casalmonferrato. In order to economise ozone De Fries obtains a more intimate contact between the water and the ozonised air by passing the emulsified mixture through a tower divided into many superposed chambers by means of finely perforated celluloid discs; the contact between the water and the ozone may be prolonged by diminishing the influx, and therefore the rate of outflow, of both; such a plant, for treating 45,000 cu. metres per day, was erected in Petrograd in 1910.

It was shown by numerous experiments in 1906–1909 that the ultra-violet rays have a bactericidal action, and that water can be sterilised by passing it over a mercury lamp emitting light rich in these rays.[1] Some French chemists maintain that the phenomenon

---

[1] **ULTRA-VIOLET RAYS.** The invisible rays of short wave-length (0·4–1 micron) beyond the violet rays of the spectrum are able to influence a photographic plate (Draper, 1874) or to cause chemical reactions. These ultra-violet rays are called chemical or active rays, although all light rays have such properties to a greater or less extent. Artificial light, especially that of an arc with metallic electrodes, gives a spectrum rich in ultra-violet rays. Way (1860) constructed the first lamp with mercury electrodes, but his experiments cost him his life. In

is due to a specific action of the ultra-violet rays, whilst many German chemists hold that the sterilisation is consequent on the formation of ozone and hydrogen peroxide, which are produced by the action of the ultra-violet rays on air and water. Billon and Daguerre

---

1879 Rapieff patented a mercury lamp, but this was unsuccessful. L'Arous in 1892 showed that, in a tube devoid of air, mercury vapour becomes luminous when a continuous electric current is passed through it, the light being very rich in ultra-violet rays. P. Cooper-Hewitt (1901) and Pawech (1904) constructed powerful mercury lamps for industrial uses (*e. g.*, public or private lighting, for which they are economical, although the light is greenish and gives people a death-like appearance; glass of suitable colour remedies this).

These lamps are constructed by the Westinghouse Company, and are tubular (Fig. 79) with terminal enlargements communicating with two small tubes full of mercury, into which dip the poles of the current source. When the evacuated tube is placed horizontal, the mercury collects at the two ends; the circuit is then closed and the tube gradually inclined until a thin stream of mercury flows from one end to the other. The current which immediately flows heats the thread of mercury and evaporates it, the current then meeting less resistance and flowing through the mercury vapour, which becomes incandescent; when the tube is brought again to the horizontal position, the emission of light continues as long as the current passes.

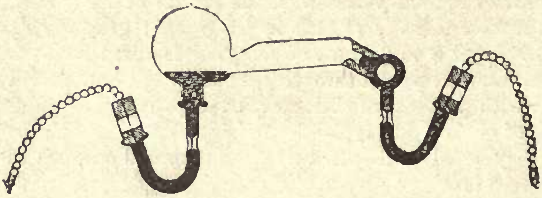


FIG. 79.

These rays injure the crystalline lens of the eye and also the epidermis; the eyes may be protected by a special yellowish-green glass (euphos) which retains the ultra-violet rays. Ordinary glass absorbs part of the ultra-violet rays, whereas quartz and rock-salt allow them to pass (to a wave-length of 0·186 micron). In 1904 Messrs. Heraeus of Hanau constructed lamps with long quartz tubes (for photographic purposes, copying drawings, etc.). Schott (1904) prepared a special glass (uviol) which is cheaper than quartz and allows of the passage of rays down to 0·253 micron.

Ultra-violet rays have a marked ionising action; they cause the immediate discharge of an electroscope and render certain substances fluorescent and phosphorescent. Around a mercury vapour lamp the oxygen is ionised, especially at a low temperature; carbon monoxide is transformed into the dioxide in presence of oxygen, although in closed vessels the inverse reaction occurs; ferric salts are reduced to ferrous salts, iodides yield free iodine, chlorates and bromates are reduced to chlorides and bromides, and potassium nitrate to nitrite. All the reductions are, however, protected by the action of the ozone formed round the lamp. Formic acid and hydrogen peroxide are decomposed, a mixture of hydrogen and chlorine yields hydrogen chloride, gelatine loses its property of swelling with water and forms a germicide similar to formaldehyde, and serum albumin and egg albumin undergo coagulation, especially in presence of a trace of acid or alkali. Paper steeped in a fixed salt of phenylenediamine is turned blue by ultra-violet rays, but is insensitive to sunlight, whilst the opposite behaviour is shown if phenylenediamine nitrate is used (Schall). Colloidal substances in solution paralyse the action of ultra-violet rays.

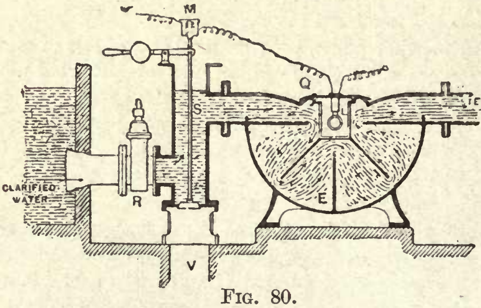


FIG. 80.

The action of the rays on zinc minerals, which are rendered fluorescent, serves for the determination of their richness and for the detection of any residual zinc in the ore residues.

In 1906 F. De Mare suggested the sterilisation of water with ultra-violet rays by immersing a mercury lamp (*see* chapter on Mercury) directly in the water and forcing the latter to flow repeatedly in a thin layer close to the lamp. Improvements in these lamps for sterilising water were made in 1908–1910 by Nogier, Thévenat, Courmont, Dornic, and Daire, that most used being the Westinghouse lamp.

An arrangement used in a series of tests made at Marseilles is shown diagrammatically in Fig. 80. Clarified water from a tank at a higher level than the lamp passes through the regulating valve, *R*, into the successive chambers, *E*, where it follows the course shown by the arrows and passes at least three times close to the quartz lamp, *L*, shown in transverse section. The water may be deviated into the discharge, *V*, by lowering the lever plug, *SM*. The hemispherical vessel is made of enamelled iron.

If butter is washed with water sterilised by either ozone or ultra-violet rays, it keeps for a long time without turning rancid.

(1910) obtained a sterilisation of water twenty-five times more efficient than that obtained with the ultra-violet rays of the mercury lamp by using the rays of the invisible spectrum between 1030 and 1100 units (Ångst.); with a special small lamp 5 litres of Seine water, containing 29,000 colonies of *Bacillus coli* per c.c., were completely sterilised per minute.

It has lately come to be considered more probable that the ultra-violet rays exert a specific action. In any case, it is indispensable that the water should be perfectly clear, since the smallest trace of suspended impurity, passing in front of the lamp, would produce a shadow which might protect some microbes from the action of the rays; filtration must, therefore, be thorough. The cost of the sterilisation is about the same with these rays as with ozone: 1 cu. metre of water requires 1–2 grms. of ozone, obtainable with 20–40 watt-hours, while, under the most favourable conditions, a mercury lamp consumes 16–20 watt-hours. In some cases, however, as much as 90 watt-hours are employed in order to ensure complete sterilisation.

WATER FOR INDUSTRIAL PURPOSES

As regards water, every industry has its own special requirements, and sometimes that which is suitable for one is fatal to another. It is, therefore, necessary to bear in mind the uses to which a given water will be put, and thus to be guided as to its goodness by the results of chemical analysis, and sometimes also by bacteriological examination. We shall enumerate briefly the principal requisites of water for certain important industries:

Boiler-feed Water should be as soft as possible and should not contain much nitrate or organic matter, in order not to form incrustations or corrode the boiler-plates (for treatment, *see below*).[1]

[1] The *total hardness* is due especially to the calcium and magnesium bicarbonates and sulphates, and is determined according to Boutron and Boudet with a titrated alcoholic solution of soap (20 grms. of potassium oleate in 520 c.c. of alcohol of 56 per cent. by volume), this being added until a persistent froth, indicating the complete fixation of the calcium and magnesium as calcium and magnesium soaps, is obtained on vigorous shaking. The titre of the soap solution is determined by gradually adding a solution of 0·574 grm. of barium nitrate (dried at 100°) in a litre of water; 40 c.c. of this solution correspond with 22 French degrees of hardness.

The *permanent* hardness is due mainly to the sulphates of calcium and magnesium, and is determined by boiling the water for half an hour, filtering and making up to the original volume with distilled water; the bicarbonates are thus removed, as they remain on the filter as insoluble carbonates.

The *temporary hardness* is deduced from the difference between the total and permanent hardness.

The burette of Boutron and Boudet for measuring soap solution indicates the results directly in grams of calcium carbonate contained in 100 litres of water, that is, in French degrees. German degrees denote the grams of calcium oxide in 100 litres of water, and English degrees the number of grains (1 grain = 0·064 gram) of calcium carbonate in a gallon of the water (1 gallon = 4·543 litres). Thus 1 French degree is equal to 0·56 German and 0·70 English degree.

If a water has a hardness of 1 French degree, the calcium and magnesium salts in a litre of it saturate 0·1 gram of soda soap (usually with 30–35 per cent. of moisture), so that a litre of a water with a total hardness of 10 will saturate 1 gram of the soap.

The molecular weight of calcium carbonate being 100, 1 degree of hardness indicates that 1 litre contains 0·010 gram $CaCO_3$, or 0·0056 grm. CaO, or 0·0111 grm. $CaCl_2$, or 0·0136 grm. $CaSO_4$, or 0·0040 grm. MgO, or 0·0095 grm. $MgCl_2$, or 0·0084 grm. $MgCO_3$, or 0·0120 grm. $MgSO_4$, or 0·0044 grm. CO_2 (2·5 c.c.).

By titrimetric analysis the approximate composition of the water may be ascertained, as shown in the following example: (1) A water showed a total hardness of 25°; (2) after treatment with ammonium oxalate (60 c.c. of the water treated with 2 c.c. of ammonium oxalate solution at 60°) and filtration, it showed 11° of hardness; (3) after being boiled for half an hour and filtered to remove the separated calcium carbonate, the water showed 15° of hardness (this would have been 12° if all the dissolved carbonate had been precipitated); (4) after treatment of this filtered water with ammonium oxalate and subsequent filtration (the calcium sulphate being thus removed), the residual hardness was 8°.

The hardness of 25° is due to carbonic acid and to salts of calcium and magnesium, and that of 11° to carbonic acid and to magnesium salts, so that 25 — 11 = 14° represents the hardness due to all the calcium salts. Hardness (3), after correction, *i. e.*, 12°, is due to magnesium and calcium salts other than carbonate or bicarbonate, whilst 25 — 12 = 13° is

Water for Breweries. The influence of the water on successful brewing is often exaggerated. Decomposing organic matter, with ammonia and nitrites and the attendant micro-organisms, is certainly prejudicial in the manufacture of beer. The lime content should be moderate, because water with little lime (little hardness) withdraws more extractive matter from the malted barley, and also more salts, including phosphates, but water containing much lime and magnesia (very hard) is harmful, because it renders the albuminoids insoluble.[1]

Water for Spirit Distilleries should be pure and cool, and should contain few micro-organisms and little $NaCl$ and $MgCl_2$.

Water for Sugar Factories. If water rich in sulphates and alkaline carbonates, and especially in nitrates, is used, the crystallisation of the sugar is rendered more difficult, molasses are more abundantly obtained, and the sugar becomes deliquescent on exposure. Water rich in micro-organisms partially decomposes the sugar.

Water for Paper Mills. The presence of iron is harmful, and an excess of lime and magnesia decomposes the resin soaps.

Water for Starch Factories. This should be free from organic matter or suspended matter. Iron is harmful and so are all kinds of algæ or bacteria.

Water for Tanneries. The bicarbonates and sulphates of lime and magnesia are advantageous because they assist the proper swelling of the hides, but when the water is less hard, thinner, softer, and neater hides are obtained. If the water contains much bicarbonate, it is sufficient to add a little sulphuric acid in order to form a little sulphate. When the water is very hard, it is better to work the hides at a tepid temperature (about 20° C.).

Water for Bakeries should be potable, and is very harmful to panification if it contains decomposing organic matter, because the action of the yeast is then notably modified.

For **Glue Factories** the water should be rather soft, as otherwise the glue is lacking in limpidity and the solutions form deposits.

Water for Laundries, public and domestic, should contain little hardness, as otherwise more soap is used and the washing is also bad.

Water for Cooking should not possess much hardness, in order that vegetables may be easily cooked.

In treating Cocoons and Silk, a water which is very soft dissolves much gummy matter and renders the silk less brilliant and resistant. On the other hand, the dyer encounters much difficulty in dyeing silk worked with very hard water, and the resulting shades are less brilliant.

Water for Dyeing should be limpid, free from iron, and should possess little hardness, as the colouring matters otherwise form insoluble lakes, producing impure shades, and sometimes also spots. In **Turkey Red Dyeing,** on the contrary, hard water is advantageous.

For **Wool and Cotton Spinning,** where the crude (wool) fibre or worked fibres (threads and tissues of wool or cotton) are washed, notable quantities of soap are wasted if the water is hard, and insoluble calcium and magnesium soaps are formed which

---

the hardness due to carbonates and carbonic acid. Hardness (4), *i. e.*, 8°, is due to magnesium salts not precipitated either by boiling or by ammonium oxalate. The sum of the hardness due to calcium and magnesium salts being 22 (= 14 + 8), 25 − 22, *i. e.*, 3, must be that due to carbonic acid. Subtraction of 3 from the 13 representing carbonic acid and calcium carbonate together leaves 10 due to calcium carbonate. Further, 14 − 10 (= 4) is the hardness due to calcium sulphate, or rather to salts of calcium other than carbonate and bicarbonate.

Thus the chemical composition of the water, excluding sodium and potassium salts, is :

Free carbonic acid = 3 × 0·0014 = 0·0132 grm. (15 c.c. CO_2) per litre.
Calcium carbonate = 10 × 0·010 = 0·100 ,, ,,
Calcium sulphate = 4 × 0·0136 = 0·0544 ,, ,,
Magnesium sulphate = 8 × 0·0120 = 0·096 ,, ,,

Total hardness = 25 Total 0·2636

[1] These views are scarcely those of the majority of brewers. Burton ales are brewed with a water containing a very large proportion of gypsum, as well as other salts, in solution.—*Translator.*

adhere tenaciously to the fibre, producing serious difficulty in dyeing and communicating a rancid odour to the tissues when they are stored for long in hot warehouses.

Each degree of total hardness causes a useless and harmful consumption of 100 grams of sodium soap (calculated with 30 per cent. of moisture) per cu. metre of water; softening a water of hardness 20 to hardness 5 effects a saving of 1·5 kilos of soap per cu. metre.

TREATMENT OF WATER FOR INDUSTRIAL PURPOSES. If water for feeding boilers has more than 15° of total hardness, it is necessary to correct this in order to hinder or prevent the incrustations which are formed on the internal walls of the boiler (boiler scale).[1]

---

[1] On heating the soluble bicarbonates of the alkaline earths, we separate the corresponding insoluble carbonates in the form of a white powder. Furthermore, as the water gradually evaporates and new water is introduced into the boiler, to be evaporated in turn, the soluble salts are also concentrated more and more, and then commence to separate. For this reason calcium sulphate is abundantly formed in powder and more or less thick and hard scales; SiO_2, Fe_2O_3, organic matter and fatty acids derived from the lubrication of the feed-pumps, are also deposited.

Even a thin incrustation renders the boiler a bad conductor of heat. Thus more fuel and higher temperatures are required to evaporate the same quantity of water. Scales 1 mm. thick cause a 10 per cent. greater consumption of fuel, and when the thickness is as much as 5–6 mm. 40–50 per cent. more fuel is consumed. Sometimes the heat is sufficiently great to render the boiler-plates red hot, and in this way they are easily worn out. If at such moments a part of the incrustation is detached, the water coming into immediate contact with the red-hot plate instantly produces so much steam and pressure that in certain cases explosions are caused. The powdery sediments are carried over by the steam and obstruct the pipes and lodge in working parts of the engine, in contact with which they cause continuous abrasion.

The cleaning of an incrusted boiler is a laborious and long operation, and also interrupts the work and damages the boiler itself, the blows of the hammer necessary to loosen the scale injuring the plates.

When part of the boiler water is not discharged at frequent intervals (every two or three days), the salts become so concentrated as to be harmful and a water softened with excess of sodium carbonate may form caustic soda, the ferric hydroxide or magnesium hydroxide (derived from magnesium carbonate by loss of CO_2—which, especially in the nascent form, causes corrosion of the boiler) decomposing sodium carbonate.

The separation of calcium sulphate as an incrustation occurs after that of the carbonates, silicates, and iron, and is due, not to the temperature (140° or even 180°), but to the concentration of the salts in the boiler.

With water concentrated in boilers, it is always necessary to determine, in addition to the total alkalinity, that due to NaOH, which readily causes corrosion. Cribb and Arnaud (1905), however, showed that corrosion of iron is more easy when the alkalinity falls below a certain limit, *e. g.*, 500 grms. of NaOH or 1 kilo of Na_2CO_3 per cu. metre of water in the boiler.

When treated with sodium carbonate, waters containing sulphates yield sodium sulphate, which accumulates in the boiler and may deposit crystals in the cold; reduction of such incrustation in contact with flame or hot gases has sometimes given rise to sulphides which attack the metal.

Although it may not form incrustation, a water which is properly softened and faintly alkaline may corrode the metal plates if it contains nitrites, nitrates, bicarbonates, ammonium salts, magnesium chloride, sulphate or carbonate, or atmospheric oxygen. Chlorides in general are not harmful if air does not enter the boiler along with the water, but magnesium chloride attacks iron forming $FeCl_2$, since iron at above 100° decomposes water to a minimal extent, forming hydrogen and ferrous hydroxide, the latter with $MgCl_2$, then giving $FeCl_2 + Mg(OH)_2$; this injurious action of magnesium chloride is exerted even at temperatures only slightly above 100°. Other magnesium salts are not harmful if the water is alkaline.

In presence of chalk ($CaCO_3$) at a high pressure in the boiler, dissolved magnesium salts separate first as basic magnesium carbonate, $Mg(OH)_2$, $MgCO_3$, which then gives $Mg(OH)_2$ and free CO_2 (at 10 or, more readily, at 15 atmos.): $MgCl_2 + CaCO_3 = CaCl_2 + MgO + CO_2$. Such precipitation of the magnesium prevents the action of the chloride on the iron, which may, however, occur if the quantity of magnesium salts exceeds four times that of the calcium carbonate. With boilers fed with sea water, chalk must be added.

Water containing fats is also to be discarded, since it forms lime and magnesia soaps, which adhere to parts of the inner wall of the boiler which are not washed by the water and are hence acted on the more readily.

If a water containing dissolved silica in presence of chlorides and nitrates is used in boilers working at about 10 atmos., hydrochloric and nitric acids are liberated, and these produce intense corrosion, while the residual water in the boiler finally becomes acid; the remedy in such a case is addition of caustic soda.

Discharge of Boiler-water. It was formerly thought that incrustation could be avoided merely by decomposition of the calcium and magnesium bicarbonates in the feed-water heater

In order to soften hard water, the numerous substances (water softeners) which one is advised to add directly to the water of the boiler are not generally to be recommended, because they are often useless or even harmful. The only one which has given good results is sodium carbonate, which forms powdery $CaCO_3$ and Na_2SO_4 with the $CaSO_4$ present.

Also ammonium chloride appears directly to retain $CaSO_4$ in solution or to dissolve it when already deposited. It acts, however, incompletely and is harmful to the bronze portions of the valves. Stannous chloride transforms calcium salts into $CaCl_2$, forming stannous oxide, but is very dear. Barium chloride separates sulphates very well from tepid water in the form of powdery $BaSO_4$, which is readily deposited, and after emptying the boiler this can be removed with a jet of water.

It is, however, more rational and convenient to separate the principal incrusting agents before introducing the water into the boiler.

Kolbe proposed to add the necessary quantity (determined by analysis) of caustic soda dissolved in water, and thus to separate the bicarbonates and sulphates according to the following reactions, which, however, are very slow and occur best on heating:

$$(a)\quad Ca(CO_3H)_2 + 2NaOH = CO_3Na_2 + CaCO_3 + 2H_2O.$$

$$(b)\quad CaSO_4 + CO_3Na_2 = SO_4Na_2 + CaCO_3.$$

For economy, and in order to avoid heating, it is better to add lime-water in order to diminish the temporary hardness, and at the same time to use a solution of sodium carbonate to diminish the permanent hardness. Calculated quantities of clear lime-water are added, remembering that an aqueous solution of lime-water, saturated and clear at ordinary temperatures, contains 1·3 grms. of $Ca(OH)_2$ per litre, and that 0·74 grm. of calcium hydroxide $Ca(OH)_2$, that is, 600 c.c. of the clear solution, are required for each

---

prior to the entrance of the water into the boiler, the calcium sulphate being regarded as sufficiently soluble under a pressure of 4 atmos. in the boiler.

It was thought also that omission to blow off would necessitate an increased consumption of heat and a higher temperature to obtain a given steam pressure in the boiler. The rise of temperature, T, per 100 grms. of solvent is represented by the molecular elevation (E) of the boiling-point by the number of mol-ions of the various substances dissolved (m, p. 100): $T = E \cdot m$. For water, E is 5·2, so that the boiling-point of 100 grms. of water will be raised 0·5° by the presence of 0·1 mol-ion, *i. e.*, of 5·8 grms. of sodium chloride, 14·2 grms. of sodium sulphate, etc.; since, however, the rise of temperature increases with the degree of ionic dissociation, these amounts become reduced to 3·3 and 9 grms. for sodium chloride and sulphate respectively. If the water in the boiler working at 10 atmos. corresponds with such concentrations, the temperature will be 180·5° instead of 180°. Thus, only an extra quantity of 0·5 Cal. per kilo of water is required, and since the heat of evaporation diminishes with rise of temperature, the increased consumption of heat is only $\frac{1}{16}$ of a Cal., or 0·025 per cent. of the total heat (which is 640 Cals. if water at 20° is used). Hence, the harm done by excessive concentration of the salts in a boiler water must be sought in the ease with which froth is formed and drops of water charged with salts are carried over with the steam.

Divergent opinions still exist as to the causes of corrosion and incrustation. Thus, while some experts assert that the concentration of salts in a boiler should never be greater than corresponds with a density of 2° Bé., others work satisfactorily at 8° Bé. or even higher. Some regard 1·5 kilos of soda (carbonate and hydroxide) per cu. metre as harmless, although the bronze fittings of the gauge-glass are then attacked if they contain more than 3 per cent. of zinc.

Boiler scale varies in colour from yellowish grey to black, and consists mainly of calcium sulphate which is separated in the form of gypsum, $CaSO_4, 2H_2O$, if the temperature of the boiler is below 120° (pressure less than 2 atmos.), or as $2CaSO_4 + H_2O$ or even $CaSO_4$ (anhydrite), according to the temperature and pressure in the boiler; together with $CaSO_4$, there is always $Mg(OH)_2$, and more or less calcium carbonate and alumina. Incrustations from sea water contain no $CaCO_3$, but only $CaSO_4$.

The following compositions are those of boiler scale from boilers fed with the same water and working at 6 and 12 atmos. respectively; characteristic is the disappearance of calcium carbonate and the appearance of calcium sulphate and magnesium hydroxide at the higher pressure:

	$CaSO_4$	$CaCO_3$	$Mg(OH)_2$	$Al_2O_3 + Fe_2O_3$	SiO_2	H_2O and organic matter
6 atmos. . .	55·37 %	31·20	4·50	3·12	4·20	1·51
12 ,, . .	80·76 %	0	13·95	0·96	1·56	2·28

The composition of boiler scale varies considerably, and may even extend beyond the following wide limits:

CaO, 15–50 per cent.; MgO, 1–16 per cent.; $Fe_2O_3 + Al_2O_3$, 0·5–30 per cent.; SO_3, 6–55 per cent.; CO_2, 4–35 per cent.; SiO_2, 1–15 per cent.

French degree of temporary hardness per 100 litres of water. (One French degree = 0·7 English degree.) In this way the bicarbonates of Ca, Mg, and Fe are precipitated as neutral insoluble carbonates: $Ca(CO_3H)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$; on separation the carbonates carry down with them the greater part (about two-thirds) of the suspended and dissolved organic matter, and, therefore, a little more than the calculated quantity of lime-water is always added. The water thus treated settles with difficulty, and it is convenient to filter it in order to obtain a perfectly clear liquid, the carbon dioxide lost being reabsorbed from the air and a normal taste thus imparted to the water.

By this method calcium sulphate is naturally not separated and magnesium salts only incompletely (the separation is more complete on heating).

Aluminium Sulphate, $Al_2(SO_4)_3$, is sometimes employed instead of lime and gives better results than alum, which was once used. It clarifies turbid and coloured waters very well. The bicarbonates form basic sulphate or hydroxide of aluminium in the state of a voluminous precipitate which, during deposition, carries down with it suspended and dissolved organic matter in the form of lakes. 1·2 grms. of anhydrous aluminium sulphate or 2·3 grms. of the crystallised sulphate are used for each degree (French) of temporary hardness per 100 litres of water. The reaction is as follows:

$$Al_2(SO_4)_3 + 3Ca(CO_3H)_2 = 3SO_4Ca + 2Al(OH)_3 + 6CO_2.$$

However, the permanent hardness is increased through the formation of calcium and magnesium sulphates, and this method is therefore suitable for the treatment of water for domestic use but not of boiler-feed water. The direct addition of colloidal aluminium hydroxide has also been suggested.

Charitschkoff (1910) maintains that a much more certain and convenient agent for clarifying turbid water is calcium permanganate, which at the same time sterilises it: $Ca(MnO_4)_2 = CaO + 2MnO_2 + O_3$; excess of this reagent must, however, be avoided. The water of the river Kura (Tiflis), which required a considerable quantity of alum to clarify it, is easily rendered clear by means of 0·01 grm. of calcium permanganate per litre.

In order to diminish the permanent hardness (due especially to calcium and magnesium sulphates) sodium carbonate is advantageously employed in the proportion of 1 grm. of dry (Solvay) soda for each (French) degree of permanent hardness per 100 litres of water. In the case of water the permanent hardness of which is great compared with the temporary hardness, a solution of sodium silicate (soluble glass) is advantageously used, 1·5 grms. of combined SiO_2 being employed for each (French) degree of hardness per 100 litres of water. It is advisable also to add an equal quantity of soda so that the bicarbonates may be separated better.[1]

---

[1] In 1873 De Haen advised the treatment of water by the following method, which has given good results in practice: The water is heated to 40°–50° and treated with the necessary quantity of $BaCl_2$ in order to decompose all the sulphates [2 grms. of anhydrous barium chloride for each (French) degree of permanent hardness per 100 litres of water]; lime-water is then added in such quantity that after ten minutes of vigorous stirring clearly visible flocks are precipitated. If the amount of bicarbonate is small compared with that of sulphate, the clarification requires much more time because there is a lack of $CaCO_3$, which, during precipitation, also carries down the $BaSO_4$. This difficulty is overcome by adding more $Ca(OH)_2$ and then passing CO_2 (flue gas) through the water.

To avoid the formation of froth in boilers fed with treated waters containing soda and sodium sulphate, the use of barium carbonate and calcium hydroxide has been proposed. The process would also yield clear water in less time.

Bohlig (1877), F. Fischer (1877), and Günsberg (1878) treat the water with magnesite which has been heated to dull redness. When thrown into water this is slowly transformed into $Mg(OH)_2$ (the direct use of magnesium hydroxide is now suggested), which reacts on bicarbonates (completely only on heating) in the same manner as $Ca(OH)_2$. The magnesium carbonate which is so formed reacts by double decomposition with $CaSO_4$, forming soluble $MgSO_4$ and insoluble $CaCO_3$. If the sulphate is in excess compared with the carbonate thus formed, it is necessary to pass CO_2 (flue gas) through the water to convert $Mg(OH)_2$ into $MgCO_3$; naturally this water cannot be used in the textile industries, as it would give rise to insoluble magnesium soaps.

The employment of hydrochloric acid to transform the carbonates into soluble chlorides has also been proposed, but a slight excess of HCl damages the boiler. HCl must not be employed if the water contains much magnesium bicarbonate, because the $MgCl_2$ which is then formed damages the boiler at high temperatures by liberating HCl. It is advisable to pass water treated with HCl through tubes containing lumps of limestone before its introduction into the boiler.

A practical method for determining how much lime-water and sodium carbonate are required for treating a given water is as follows: 200 c.c. of the water are titrated with clear saturated lime-water in presence of phenolphthalein until the solution turns violet. Another sample of the water, previously boiled and filtered (to eliminate bicarbonates), is titrated with standard sodium carbonate solution in presence of phenolphthalein. The amounts of lime-water and sodium carbonate required per cu. metre of water are then calculated.

In no case is it possible to eliminate completely the hardness of water even if an excess of the reagents is added, because the following reaction is partially reversible:

$$CaSO_4 + Na_2CO_3 \rightleftarrows CaCO_3 + Na_2SO_4.$$

If the treated water is left slightly alkaline, the boiler will not be attacked even if nitrates are present in excess.[1]

[1] **Notes on the Treatment of Water.** Although the one most commonly and successfully used, the Bérenger-Stingl lime-and-soda process, described above, is inadequate and somewhat inexact, since the permanent hardness is due not only to gypsum, but also to calcium and magnesium nitrates and chlorides, which cannot be eliminated with the same quantity of reagent and not always with the same reagent as is used to expel the gypsum. Thus, whilst the latter is removed as the slightly soluble calcium carbonate by treatment with sodium carbonate, magnesium chloride and sulphate cannot be separated as carbonate (which is somewhat soluble), but are best thrown out as the less soluble hydroxide, $Mg(OH)_2$. Further, whilst magnesium chloride may be removed by means of caustic soda [$MgCl_2 + 2NaOH = 2NaCl + Mg(OH)_2$] or calcium hydroxide [$MgCl_2 + Ca(OH)_2 = CaCl_2 + Mg(OH)_2$], magnesium sulphate is best expelled by treatment with baryta, with which it forms two insoluble salts [$MgSO_4 + Ba(OH)_2 = BaSO_4 + Mg(OH)_3$].

If, then, treatment of the permanent hardness is based on the titration results (with soap solution), the above considerations are left out of account and the treatment is inexact. Another source of slight error consists in omission to allow for the free carbonic acid always present in water; this is scarcely ever determined and escapes the soap test, whereas in practice it fixes a certain, although small, quantity of calcium hydroxide as insoluble carbonate.

A far more rational and reliable method, proposed by Wehrenfenning, by Blacher and by Hundeshagen, consists in establishing, on the basis of the analytical results, the hardness equivalents of the separate salts present with respect to the reagents to be used in the treatment.

When these hardness equivalents are once ascertained, it is possible to derive general formulæ by which the quantities of the different reagents, necessary to give the best results in any case, may be calculated.

The hardness (French degrees) corresponding with all the calcium salts expressed as carbonate may be represented by the symbol *Hca;* that corresponding with all the magnesium salts expressed as $CaCO_3$ by *Hmg;* and those corresponding with the bicarbonates, free carbonic acid (as $CaCO_3$), and sulphates (as $CaCO_3$) by *Hbi*, Hco_2, and Hso_3 respectively. In order to calculate the quantities of the separate reagents to be added, use is made of the following equivalents, representing the quantities of the reagents corresponding with 1° of hardness per cu. metre of water: calcium hydroxide, 7·4 grms. (*i. e.*, 5·7 litres of clear, saturated lime-water); sodium carbonate, 10·6; barium chloride, 20·6; barium carbonate, 19·6 and barium hydroxide, 17 grms.

Various general formulæ have been suggested (Kalmann, 1890; Pfeifer, 1895 and 1902; Thiele and Flad, 1906, etc.), one of the most complete and rational being that of Hundeshagen (1907), illustrated by the following example. Given a water for which $Hca = 17$, $Hmg = 9·5$, $Hbi = 18$, $Hco_2 = 2·6$ and $Hso_3 = 7·7$, treatment by the lime-soda method is carried out in accordance with the two formulæ:

I. 7·4 ($Hmg + Hbi + Hco_2$), *i. e.*, 7·4 (9·5 + 18 + 2·6), = 223 grms. of $Ca(OH)_2$, or 172 litres of lime-water.

II. 10·6 ($Hca + Hmg - Hbi$), *i. e.*, 10·6 (17 + 9·5 − 18), = 90 grms. of Na_2CO_2. Each cu. metre of this water thus requires 90 grms. of soda and 172 litres of lime-water.

If the lime-barium chloride method is used, formula I. remains as above, whilst II. becomes: 20·6 Hso_3, *i. e.*, 20·6 × 7·7 = 158·6 grms. of $BaCl_2$.

If the lime-barium carbonate process is used (*see later*), formula I. remains unchanged and II. becomes: 19·6 Hso_3, *i. e.* 19·6 × 7·7 = 151 grms. of $BaCO_3$.

The materials used in these three processes cost about 0·15*d.*, 0·3*d.*, and 0·2*d.* respectively. Precipitated barium carbonate must be used, not the ground natural product (witherite).

Even when applied on the basis of the hardness equivalents, the lime-soda process still presents a weak side when it is a question of eliminating the sulphates which cause permanent hardness and the corresponding scale. The sodium sulphate formed by the action of sodium carbonate on gypsum is extremely soluble, but it accumulates as evaporation proceeds and results in increased expenditure of fuel and in corrosion of the metallic connections, so that the boiler must be emptied completely from time to time. An ideal purification would eliminate from the water all the salts which form scale without leaving others in solution.

On these considerations is based the method of purification by means of barium salts. Barium chloride (suggested by F. Kuhlmann in 1841 and again recommended by De Haen

Of great interest is the Gans process, which not only softens water, but also frees it from manganese and iron. Gans (1907) showed that, when water is passed through a layer of powdered artificial zeolite, *i. e.*, sodium silico-aluminate (prepared by fusing together 6 parts of quartz sand, 3 parts of kaolin, and 12 parts of sodium carbonate and afterwards washing with water; according to German patent No. 200,931, 1907, the sodium carbonate may be replaced by a mixture of sodium bisulphate and coal), the water gives up all its lime and magnesia in an insoluble form and takes in their place a corresponding amount of soda. Hence the water loses all its temporary and permanent hardness.[1] In some cases, however, the water retains soluble magnesium salts (it is then somewhat turbid), which do not give boiler incrustation when calcium salts are lacking.

Various artificial zeolites are sold by Messrs. J. D. Riedel (Berlin) under the name *permutite* in pale grey porous lumps. Natural zeolites effect only minimal purification. When the artificial zeolite is exhausted by use, *i. e.*, when it has exchanged all its alkalies for lime, magnesia, iron, etc., it may be rendered active again by passing through it a solution of sodium chloride from which it fixes the sodium, giving up the calcium, iron, etc. For turbid waters, even after filtration, the permutite process is not to be recommended. In order that water may not become too alkaline in the boiler and may not exceed the density 2–3° Bé., the frequent discharge of the residual water is necessary.

---

in 1873) separates the sulphates completely, but leaves the soluble calcium chloride in solution. More rational is the use of barium hydroxide (proposed by Parker in 1826, but applied only later), which allows of the complete elimination of the permanent and temporary hardness without the introduction of new soluble salts :

$$CaSO_4 + Ca(HCO_2)_2 + Ba(OH)_2 = BaSO_4 + 2CaCO_3 + 2H_2O.$$

This ideal process (except that it is slightly more expensive than the lime-soda method), like that in which barium chloride is used, presupposes, however, that the degrees of permanent and temporary hardness are equal; this is not often the case. If the permanent hardness is the greater, calcium hydroxide will be left in solution : $CaSO_4 + Ba(OH)_2 = BaSO_4 + Ca(OH)_2$.

The use of barium carbonate alone was suggested in 1859 by E. Wurtz and has again come under consideration during recent years, although the repeated practical tests made in the meantime have been uniformly unsuccessful. Barium carbonate is almost completely insoluble in water (0·007 per cent.), and, when used in a finely divided condition and in large excess, separates almost the whole of the calcium and magnesium salts (especially if a little calcium hydroxide also is added when the water is very rich in bicarbonates) constituting the temporary and permanent hardness :

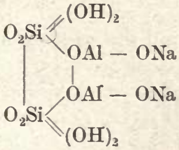
$$CaSO_4 + Ca(HCO_3)_2 + BaCO_3 + Ca(OH)_2 = 2H_2O + 3CaCO_3 + BaSO_4.$$

Any excess of barium carbonate remains undissolved, and its power of reacting gradually increases as the precipitated salts are deposited.

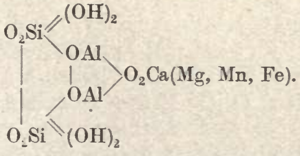
Messrs. H. Reisert (Cologne) have taken out patents in 1902 and succeeding years for automatic plant with special arrangements for the periodical removal of the excess of fine barium carbonate, which is introduced in quantities sufficient to last two or three months.

Barium carbonate costs less than sodium carbonate (more is, however, consumed, owing to the higher molecular weight) and allows of even very hard waters being softened to not more than 4 degrees of hardness. Calcium chloride, which seldom occurs in water and forms no scale, but consumes soap in the washing of textiles, is not precipitated by barium carbonate.

[1] Since permutite allows of the reduction of the hardness of water to zero, its use is of importance not only for boiler water, but also in all textile industries in which soap is employed. To artificial zeolite Gans attributes the structure :



$+ 3H_2O$; after reaction with calcium, magnesium, and manganese salts, the structure is probably,



The use of permutite has also been proposed in sugar factories to remove the potassium salts of the sugar juices and thus allow of complete crystallisation of the sugar; further, the potassium salts of molasses may be replaced by sodium salts and thus rendered more appetising to cattle, the sodium of the zeolite being replaced by potassium.

AUTOMATIC PLANT FOR THE PURIFICATION OF BOILER-FEED WATER. Many forms of plant have been proposed, but they are almost all based on the idea of passing simultaneously through a pipe a definite quantity of water and a corresponding quantity of solutions of sodium carbonate and lime-water in the proportions required by the permanent and temporary hardness of the water under treatment. The plants of Gaillet, Dervaux, Dehne, etc., are much used. Figs. 81 and 82 illustrate Dervaux's plant. The water passes into the vertical pipe *E* from the pipe *P*, which is connected with the main, *A*, and is automatically regulated by means of floats. Clear lime-water passes simultaneously through the tube *U*, which is fed by the reservoir, *S*. By means of the siphon, *QN*, sodium carbonate solution also passes in from the vessel *B*, which is fed by the reservoir, *C*. The mixture is homogeneous and the sulphates and carbonates which are precipitated collect at the bottom of the large reservoir, *D*, and may be removed from time to time through the cock *O*. The turbid water is clarified by passing slowly and by a lengthy path along the numerous inclined plates, *M*, which are fixed in the large vessel, and the deposit continually falls to the bottom. In order to obtain the water in a perfectly clear condition it passes through the filter, *F*, formed of a compact layer of beechwood shavings, before issuing from the tube *T*. The sodium carbonate solution is maintained at a constant concentration because there is always an excess of solid sodium carbonate in the perforated container, *Z*. The lime-water is prepared in the conical tank, *S*, at the bottom of which quicklime is introduced through the tube *J*, and the water entering through the tube *V* becomes saturated and clarified as it rises. The final suspension of fine calcium carbonate which is always present, together with the lime, is deposited in the cone, *K*, and removed through the tube *G*. The insoluble impurities in the lime are removed through the cock *L*. The course of the water from *H* to the exit, *T*, takes more than an hour, and thus it is well clarified. Plants are built to produce 50, 100, and even 200 cu. metres of purified water per day, and the velocity of the water in the plant is regulated in such a manner that it issues in a clear condition.

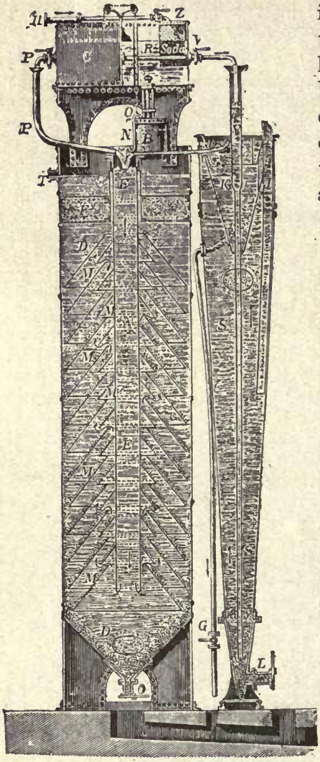


Fig. 81.

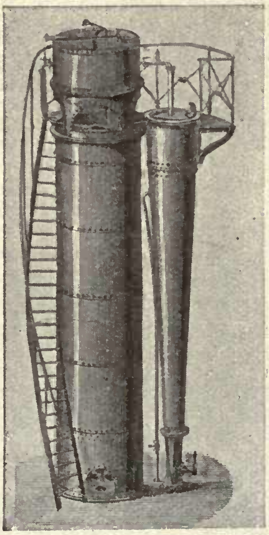


Fig. 82.

Gaillet's plant is very similar to that of Dervaux, but the lateral tank containing lime is dispensed with, and the lime-water is prepared in a small vessel above and close to that in which the soda solution is prepared. In other plants the vessel in which the lime-water is prepared is placed centrally inside the purifying tower. Finally, some plants are fed with the exact quantity of sodium carbonate necessary by means of a bucket wheel the velocity of which can be modified as desired.

ELIMINATION OF ORGANIC MATTER. If this is suspended, or even in solution, the use of metallic iron is advisable. With water this forms ferric hydrate, which separates almost all the organic matter. In 1892 Piefke proposed to pass the water through a revolving drum containing spongy iron or iron turnings. In Paris 4000 cu. metres of Seine water are treated per twenty-four hours by means of 2000 kilos of iron by Anderson's process. The same Anderson process is also used at Monaco, Antwerp, Montevideo, etc. The organic matter which gives water a yellowish tint is readily separated by addition of a powdered mixture of chalk and a ferric salt, followed by filtration.

SEPARATION OF IRON FROM FERRUGINOUS WATERS. All waters contain combined iron, but as ferruginous are regarded only those which deposit their iron as hydrated oxide when left in contact with the air for a few minutes or hours or when heated. The amount of iron in these waters always exceeds 0·35 mgrm. of ferric oxide per litre.

It was at first thought that it would suffice to aerate such water vigorously to cause immediate separation of the iron and then to clarify it (Salbach, 1868; Auklam, 1880; Wingen, 1882). In 1890 Oesten proposed to drop the water from a height in the form of a fine shower, and in many cases this procedure gave excellent results. In other cases, however, despite all precautions, the water remained yellowish and opalescent. It is evident that the iron is not chemically combined always in the same way, and the various sources of the iron may be considered.

If water flows over the surface of soil rich in iron minerals, the latter are dissolved either not at all or in negligible traces, and even if it already contains dissolved iron salts these are separated under such conditions. In traversing the superficial layers of the soil, the water becomes enriched in carbon dioxide, derived partly from the air and partly from the decomposing organic matter of the soil. If it then penetrates into the deeper strata, far from contact with the air, and there meets iron minerals, relatively large proportions of iron (up to 0·1 gram per litre) are dissolved as iron bicarbonate. Further, if these deeper layers also contain decomposing organic matter (peat, etc.), more complex compounds of iron with a basis of organic acids (humic acid) are formed, together with hydrogen sulphide and ammonia resulting from the decomposition of the proteins of the organic matter. In some cases these layers exhibit very active bacterial growths, which produce carbon dioxide, while in iron pipes abundant development often occurs of iron algæ (*Crenothrix*, *Chlamydothrix*, *Gallionella*, etc.); these grow anaerobically and contribute notably to the attack of iron or its ores, the iron they assimilate being afterwards given up to the water as soluble salts.

When air acts on a water containing iron organically combined, the oxygen first oxidises the organic matter, so that simple aeration does not always eliminate the iron immediately.

In 1891 Piefke proposed that the aerated water be passed through coke or stones so as to induce rapid separation and precipitation of the iron, which is transformed by air into the colloidal hydrated oxide. Dunbar and Kryck (1898) made the interesting observation that the effect of the coke or stone increased with increase of the layer of hydrated oxide of iron deposited on it. This oxide acts, indeed, as a catalyst, fixing the oxygen of the air and transferring it at the same time to the oxidisable substances of the water (iron in various forms of combination).

Kröhnke obtained a better initial effect by soaking the coke previously in ferric chloride and calcium hydroxide and thus depositing on it finely divided hydrated oxide of iron, which multiplies enormously the surface of contact with the colloidal hydrated oxide of iron in the water and causes its separation by true colloidal action.

The water itself may also be treated directly with about 10 grams of ferric chloride and then 50–100 grams of lime (slaked with water) per cu. metre. Deposition of the flocculent ferric hydroxide thus formed causes separation not only of the dissolved iron salts, but also of part of the calcium carbonate, while the organic matter, colouring substances, etc., are also carried down, the water being clear and colourless after filtration through sand.

In 1900 Schindowsky showed that in every case the whole of the iron may be expelled from water by treatment with a sufficient excess of air, and in 1904–1908 Bock, Deniss and Jacobi, Halvor Breda, and Darapsky devised very simple and convenient closed sand filters, consisting in some cases merely of an iron tube inserted in the piping leading to the cistern; into this tube the water is injected under pressure along with excess of air (up to 40 per cent. of the water by volume), the velocity of the water being regulated according to the surface of the filtering mass and to the quantity of air injected. This procedure results in the removal, not only of the iron, but also of all the iron algæ (*see above*), which would otherwise multiply in the cisterns and piping and cause obstruction, Mertens (1904 and 1907) aerates the water by centrifugation.

In recent years iron has been successfully eliminated, even in difficult cases, by the manganese permutite process (*see below*).

During the last few years, various processes have been invented, but good results have been obtained with plant of the type here described, which represents that erected in 1903 at Frankfort-on-Oder by the Städtereinigungs Gesellschaft of Wiesbaden for ferruginous water obtained from a peaty subsoil. The water of these soils, which is yellowish and opalescent, is raised by means of a pump to the top of the tube *L* (Fig. 83) and is then distributed by ramified tubes over a perforated plate, *A*, which subdivides it into a fine spray, on to a layer of gas coke in large pieces, *B*, contained in a sort of stout galvanised iron wire cage, *E*, about one metre high in such a way that air circulates through the coke in every direction, energetically oxidising the iron dissolved in the water and separating it in the form of insoluble oxide.

After passing over this first layer the water is poured in the form of spray over a second layer of coke not indicated in the figure, and then, still as a spray, *D*, through which much air passes continuously, it falls into the tank *C*, which is always kept full so that the water may penetrate through the rapid Kröhnke filters full of sand, issuing as a clear liquid from the central tube of the same filter and collected in the tank *F*.

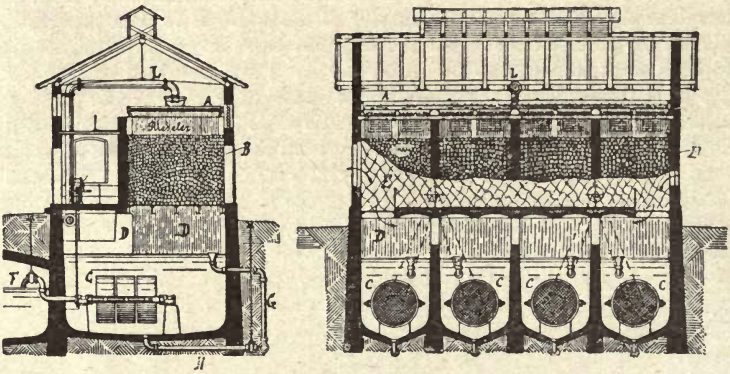


FIG. 83.

The deposits from the tank *C* are always able to escape by the tube *H*, and the excess of unfiltered water passes away through the tube *G*. When the filters are obstructed, they are washed with an abundant supply of water, being kept in motion meanwhile in order to stir up the sand of the filter.

In cases in which humic substances are abundant, the separation of iron from the water is more difficult and necessitates repeated treatment. The separation of the iron occurs more easily when the carbon is coated with ferric hydroxide, because it is this substance which acts catalytically, yielding oxygen to oxidise the humic substances and being continually regenerated by means of the atmospheric oxygen (hence the aeration). For this reason the addition of ferric salts to the filter or contact medium is often advised. We have seen on p. 109 how the study of colloidal solutions may also serve to explain this process of the separation of iron from water.

From manganiferous waters (these are often found, and some years ago the water of the Breslau aqueduct suddenly exhibited a high content of $MnSO_4$ and turned brown in the air with formation of a brown deposit) and ferruginous waters the manganese and iron may be separated (besides by aeration) by means of permutite (*see above*). The water is passed through a filter consisting of a layer 60–80 cm. thick of powdered artificial manganese zeolite, prepared (Gans process) by fusing a calcium silico-aluminate with $MnCl_2$ and transforming the manganese radicle into Mn_2O_7 by treatment with sodium or calcium permanganate. The MnO of the manganous compounds of the water is oxidised by the Mn_2O_7 and separated as insoluble MnO_2, which is retained by the filter. When the Mn_2O_7 has given up all its active oxygen, the filter is exhausted, but the Mn_2O_7 may be regenerated and the filter reactivated by treatment with sodium or calcium permanganate solution. Purification by this method costs 0·3*d.* to 0·5*d.* per cu. metre of water.

The separation of iron is effected by the same zeolites as remove manganese, since Mn_2O_7 is an energetic oxidiser also of organic iron and separates it as flocculent oxide, which is retained by filtration.

PURIFICATION OF EFFLUENT WATERS

With the progress of chemical industry and increase of population in large centres, the establishment of hygienic standards became necessary for the protection of the public health. The large drainage systems of the cities did not suffice, because the sewage water often defiled the watercourses and carried infection even to great distances. It was thus necessary to have recourse to a system of rational purification of effluent and sewage water. Mere clarification did not suffice, because organic matter remained dissolved, and this easily underwent putrefaction and became dangerous to vegetation and to fish life. Even chemical precipitation is not always sufficient because lime, aluminium sulphate, and ferrous or ferric sulphate or calcium hypochlorite separate only the coagulable albuminoids and suspended matter, and the quantities of sludge produced are very large and are not willingly employed by agriculturists: at Leipzig 2,000,000 cu. metres of effluent water are purified in this way per annum, 8,000,000 kilos of iron sulphate being consumed and 100,000 cu. metres of mud produced. During the last few years good results appear to have been obtained with colloidal ferric hydroxide in the proportion of 1:1000 which is completely precipitated, carrying down a large part of the organic matter. This process is, however, neither practical nor economical, and does not solve the sludge problem. True purification is obtained only when all the organic matter is decomposed and transformed into nitrates, N, CO_2, H, hydrocarbons, etc.

Certain micro-organisms are able alone to produce such a transformation and it is actually to these that the decomposition of stable manure distributed on the fields and of the corpses in the cemeteries is due, and the same is the case with the natural purification of the waters of rivers into which the sewage of cities is discharged.

Ternary compounds (organic compounds of C, H, and O) are destroyed more especially by aerobic bacteria, which when present in water are obliged to obtain the oxygen which they require from the organic matter which is present, thus decomposing it. Quaternary organic substances (containing also nitrogen) are gradually decomposed by various anaerobic and aerobic bacteria, the albuminoids being first transformed into peptones and amino compounds, and these then into ammonia, nitrites, nitrates, methane, N, H, and CO_2.

It is thus not easy to provide for the purification of the immense quantities of water which accumulate in the sewers of populous cities. One need only remember that Paris with its system of "tout à l'égout" daily produces 1,000,000 cu. metres of sewage water which cannot be passed into the watercourses without having undergone purification, because each litre of this water contains 1·250 grms. of dry residue, two-thirds of which consists of mineral matter and one-third of organic matter. London separates weekly from 80 to 100 tons of bulky detritus and floating bodies in its sewage water, and also Milan[1] and all important cities have to devise some method of purifying the water from

---

[1] In 1904 the sewers of Milan collected the refuse of 150,000 inhabitants, the new drainage works being still incomplete, and this was distributed over 2800 hectares of ground (6830 acres), of which 2000 formed a sewage farm. When the drainage scheme is complete, an area of irrigated ground of 1 hectare (2·44 acres) will be used per 300 inhabitants. In 1902, however, Menozzi recommended the employment of 1 hectare of ground for every 90 inhabitants (in any case not more than 150 inhabitants) in order to unite the maximum hygienic advantage with the greatest agricultural profit. In 1907, 5000 hectares (12,200 acres) of land were already used for the deposition of the Milan sewage, and by 1914 this had risen to 8400 hectares 20,500 acres), while a further 4000 hectares (9760 acres) is channelled ready for future use.

The farms which are irrigated with the sewage water now give eight or even ten crops of grass per year, and every hectare produces on an average 300 quintals of hay per annum. It their sewers. During the last quarter of a century collection of the favourable results obtained in Paris and Berlin by a simple and very economical system of purification has commenced. The sewage water is distributed over immense surfaces of cultivated ground, or simply of ploughed land, which retains the fertilising principles, and the water is collected at a depth of a few metres in enormous drainage tubes and is clear and relatively pure. The City of Berlin has already devoted to this purpose 11,000 hectares (26,800 acres) of land, and in Paris a smaller area, 3700 hectares (9000 acres) under vegetables and 1800 hectares (4400 acres) of meadow, are employed, but these are subjected to more intense cultivation, so that 40,000 cu. metres of water are passed per year over each hectare (2·44 acres) of land. In order to avoid saturation or obstruction of the soil, the irrigation is interrupted during twelve hours in the twenty-four, and for some days in the week, so as to allow the chemical-biological phenomena to take place more rapidly, because on these phenomena, in which not only chemical and mechanical processes but more especially the life processes of the aerobic bacteria take part, the proper purification of the sewage water depends. Pucch showed in 1908 that even as much as 600,000 cu. metres of sewage water (first roughly filtered) can be passed over each hectare of land per annum.

A new process, called the biological process, which has greatly extended during the last few years, is merely an improvement of that already described, and the decomposition of the noxious substances is carried out progressively by relying upon various species of micro-organisms at various periods. In this way these co-operate in a marvellous manner to perform their purifying work. We give a sketch of an installation (visited by the writer) erected in 1902 at Grünewald, a suburb of Berlin, erected by the Städtereinigungs Gesellschaft of Wiesbaden, to purify the effluent sewage water from one part of the quarter and the large quantities of washings from the cattle wagons in the adjacent railway station before these are turned into the outlet canal.

The water enters by the pipe *O* into a sand-filter, and then into a reservoir of masonry sunk into the ground and covered by a vault and divided into three chambers (septic

---

is found advantageous to interrupt the irrigation for a few days occasionally in order to give the bacteria time to decompose the substances deposited on the surface and in the interior of the soil. Rigorous inquiries conducted in various countries and also in Milan show that the regions in which sewage farms are placed have not been subject to any epidemics proceeding from this cause. Even the animals fed on the fodder from these meadows do not suffer any ill results (experiments conducted in Berlin in 1907). The ammonia, hydrogen sulphide, suspended matter and alkaline reaction which are always found in sewage water are destroyed by this purification, and the organic nitrogen and phosphoric acid are markedly diminished. Effluents containing 10,000,000 of bacteria per c.c. contain less than 400,000 after the third day of culture.

It has been calculated that the sewage water of Milan in 1914 measured about 4000 litres per second, 2600 from the consumption of drinking water and 1400 taken from the Naviglia to dilute it; in rainy weather, however, the principal sewage collector may receive 70,000 litres per second. Milan sewage is more dilute (0·02–0·03 grm. of organic nitrogen per litre) than that of Paris (0·06–0·07 grm.), where street cleaning is carried out on the "tout à l'égout" system, the inspection chambers thus receiving an immense amount of solid matter, which has to be removed elsewhere at a cost of 12*s.*–16*s.* per cu. metre, whereas if the streets were swept the removal would cost only 4*s.*–5*s.* per cu. metre for a smaller quantity.

The greatest purifying power is possessed by permeable, light clay soils with a subsoil of sand and gravel. If the soil is too clayey, it must be drained at a certain depth and the filtered water collected in a vessel at the lowest point and used again and again for irrigation until sufficiently purified. This is done at Leicester, where the irrigation is preceded by a partial and rapid biological purification, which eliminates many of the pathogenic bacteria, and is thus distinctly advantageous. The favourable conditions of Milan exist also at Edinburgh—where the sewage is used to irrigate the downs at Craigentinny—at Huertas (Spain), and a few other places.

In some large towns, such as Nuremberg (260,000 inhabitants), Stuttgart (177,000), etc., the great expense of a general system of sewage is avoided by transporting the contents of water-closets in tank-wagons which are filled by means of pumps, and taken 60–80 kilometres to be discharged into large cement tanks, farmers paying for them 9*s.* 6*d.*–12*s.* per wagon-load. If diluted too much with water, fecal matter rapidly loses a great deal of nitrogen (5–15 per cent. in 7 days, 22–55 per cent. in 15 days, and 80–90 per cent. in 60 days), so that at Nuremberg the liquid is decanted from the solid part as soon as this settles in the large tanks.

In order to avoid excessive dilution of the fecal matter and thus diminish cost of transport, the water of closets (5–15 litres per litre of solid and liquid excrement) is sometimes replaced by mineral oils (Vienna, Nuremberg, etc.). In some towns, *e. g.*, Posen, Avignon, Binz, and Lyons, the contents of water-closets are forced by air-pressure through iron pipes to tanks three kilometres distant.

tanks, Fig. 84: section, aspect, and plan). As the water passes slowly from the one portion into the other, the suspended organic matter is deposited and gradually putrefies through the action of the anaerobic bacteria, becoming soluble and thus more easily oxidisable. In these septic tanks only very small quantities, if any, of deposit are left.

The water is then distributed alternately to a lower level by means of automatic syphons and perforated tubes on to bacterial or oxidising beds formed of masonry chambers, at the bottom of which are perforated drainage tubes and on which lies the first layer of 30 cms. of gas coke in large pieces, then 20 cms. of medium-sized pieces, and then a third layer of 50 cms. of small coke (5 to 30 mm. diameter). At this point are placed the perforated distributing tubes, which are covered or protected by a layer of 30 cms. of coarse coal cinders.

The water which fills one of the bacterial beds remains stagnant for two or three hours, after which it is removed by means of a syphon on to a lower bed constructed in the same manner. The other upper bed is then at once filled with new water, whilst the first remains empty, so that the aerobic bacteria multiply with the help of the atmospheric oxygen, nitrifying and destroying the nitrogenous organic and ammoniacal matter retained by the coke. Thus the bacterial beds do not become obstructed and do not lose their activity. The water which issues from the first upper bacterial beds is almost clear, and when it is removed from the lower beds after about one and a half hours it is clear, colourless, and odourless, whilst the sewage water before the purification is blackish, turbid, and fœtid. The water thus purified is no longer able to undergo putrefaction.[1]

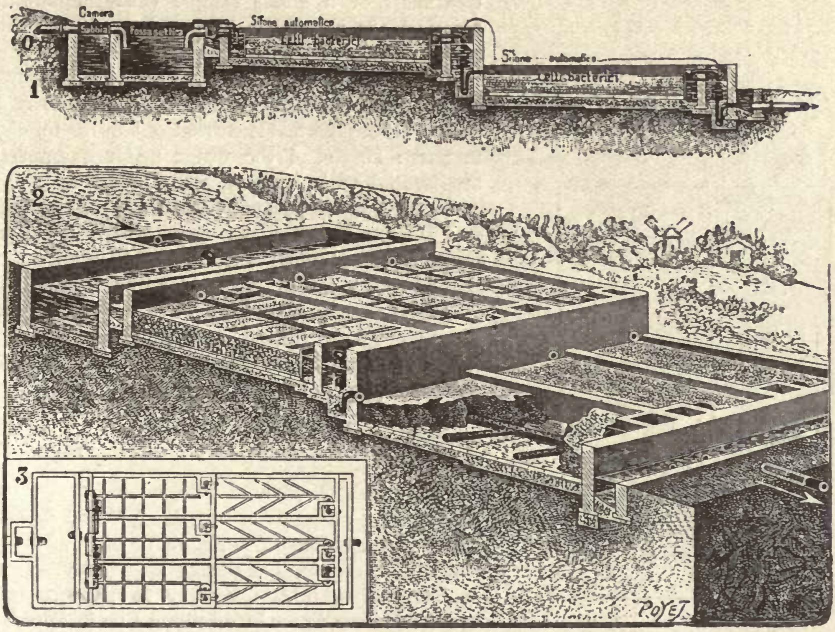


FIG. 84.

Sabbia = sand; Fossa settica = septic tank; Letti bacterici = bacteria beds.

---

[1] Exact experiments conducted under the auspices of the Berlin Municipality have shown that the sewage water contained 70 mgrms. of suspended organic matter per litre, and that after purification it contained none. Before purification it contained 30 to 40 mgrms. of ammoniacal nitrogen, and afterwards only 0·07 mgrm. The dissolved organic matter before purification was oxidised by 126 to 147 mgrms. of potassium permanganate per litre, whilst after purification only 18 to 22 mgrms. were required. The number of bacteria, which at first averaged 1,000,000 per c.c., was afterwards about 45,000. The quantity of nitrates was increased in the process through nitrification by the aerobic ferments.

In the case of epidemics it is advisable to subject such water to sterilisation by means of ozone (*see* Ozone) in order to destroy the pathogenic bacteria completely. This can be carried out at a cost of about one-third of a penny per cubic metre in the case of large installations, or even more economically by means of small quantities of calcium hypochlorite.

Each time that the water is removed from the bacterial beds, these must be left empty in contact with the air for one or two hours, in order to revive the activity of the oxidising bacteria, and the work thus alternates continuously from the one bacterial bed to the other. In England and America bacterial beds which work continuously are also much used. In these the water is distributed in the form of a very fine spray, and it is thus extensively aerated, so that a greater effect is obtained for the same surface of bed. These plants, however, are more costly and require continual repairs to the distributing apparatus.

New bacterial beds acquire their full activity only after some weeks in summer, or some months in winter. During the last few years less importance has been attached to the action of septic tanks. It has also been found that nitrifying bacteria develop quite well even on beds of peat.

In order to ascertain whether a sewage water has been purified by a biological process and has lost its tendency to putrefy (that is, to evolve an unpleasant odour and hydrogen sulphide), Spitta and Weldert in 1906 proposed the treatment of a small sample with indonaphthol blue: if the water has been well purified it does not decolorise the latter in five or six hours, but if impure it causes decolorisation even before hydrogen sulphide is formed. According to Fendler and Stüber (1909) the test is carried out in the following manner: 20 c.c. of the water under examination are treated with 1 cm. of HCl, 0·3 c.c. of a 1 per cent. solution of paraminodimethylaniline sulphate and 0·3 c.c. of a 1 per cent. hydrochloric acid solution of sublimed ferric chloride (hydrochloric acid of sp. gr. 1·125); as soon as hydrogen sulphide is formed even to the extent of 0·5 mgrm. per litre, the blue colour immediately appears. Hydrogen sulphide may also be detected by means of lead acetate paper.

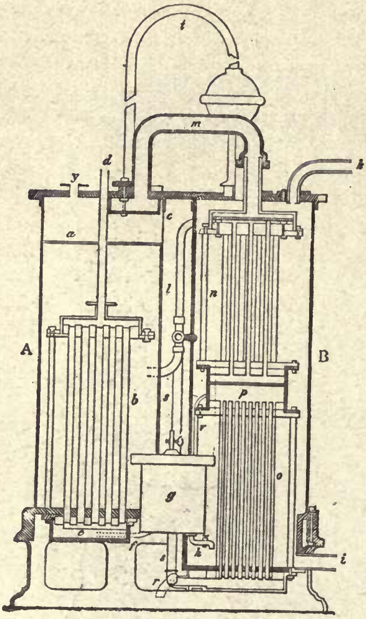


FIG. 85.

DISTILLATION OF SEA WATER

During short voyages vessels carry fresh water for drinking purposes in barrels of wood, or better still, in iron tanks. After some days, however, the water putrefies, so that during longer voyages, and in battleships, it is necessary to produce it on board from sea water by distilling this in apparatus which occupies little space and utilises the heat efficiently. It is impossible to use the condensed water from the engines for human consumption, because it contains much contamination from the evil-smelling oil with which the pistons are lubricated. As distilled water contains no dissolved air and is tasteless, it is advisable to aerate it by suitable means. The vessels of the German Navy carry plants which distil 1250, 2400, or 5000 litres per twenty-four hours, and are represented diagrammatically in Figs. 85 and 86.

They have two cylinders, *A* and *B*, of about 0·4 metre diameter. The heating and distillation of the sea water contained in *A* are carried out by a group of tubes (immersed in the water itself) in which steam circulates under pressure. This steam passes in through the tube *d* from suitable boilers, whilst the steam condensed in *e* passes into the condenser and water-separator, *g*. The steam from the sea water which is evolved in *A* passes a perforated copper diaphragm, *a*, and then another one, *c*, before entering the delivery tube, *m*, so that any small drops of water and traces of salt carried over by the steam are retained. The steam condenses in the group of tubes, *n*, of the refrigerator, *B*, and the water is collected in *p*, together with the hot water proceeding from the condenser, *g*, through the tube *v*.

The water thus condensed is completely cooled in the other group of tubes, *o*, and issues from the lower tube *r* to be used or to be passed through a carbon filter. The water from the cooler enters cold from the tube *i*, and escapes hot from the tube *k*, after which it serves to increase the water supply in *A* as fast as it is distilled. The air which is developed from the water in the refrigerator escapes from the tube *t*, and is conducted into *A*, where it mixes with the vapours of the distilled water and remains dissolved in them after condensation. The water thus obtained no longer has the disagreeable taste of boiled non-aerated water.

Pamphlette (Ger. Pat. 47,219 of 1888) distils sea water under reduced pressure and aerates it simultaneously.

H. Ferguson (Ger. Pat. 53,397 of 1889) employs steam dried before condensation, as otherwise the water has no taste.

DISTILLED WATER

For laboratory use and also for certain industries chemically pure water is required and is obtained by distilling ordinary water with suitable precautions.

The distillation is carried out in tinned copper boilers, furnished with a special still-head and with a serpentine cooler of block tin. Violent boiling is avoided in order to prevent the steam from carrying over impurities. The first portion of the distillate is rejected because it contains carbon dioxide and ammonium carbonate, which are recognised by the turbidity they produce in a solution of lead acetate. If the water contains magnesium chloride, a little lime is added before distillation in order to prevent hydrochloric acid from distilling. In this case, however, the first portion of the distillate is rejected because it contains ammonia from the ammoniacal salts: the remainder of the distillate is pure water. It is, however, necessary to leave the last portion of the water (about a quarter) undistilled, because certain organic substances commence to decompose, yielding impure distilled water.

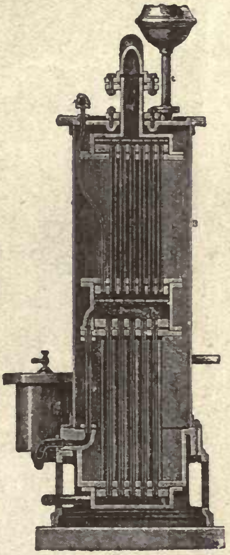


FIG. 86.

Stas added 4 to 5 per cent. of a concentrated solution of potassium permanganate to the water. He then let it stand for twenty-four hours and added a further 1 to 2 per cent. of potassium permanganate solution and as much fairly concentrated potassium hydroxide solution (in order to obtain a slower decomposition of the permanganate) before distilling. At the commencement of ebullition the heat supply was moderated because much foam was at first formed. After the twentieth part of the water had passed over he commenced to collect pure distilled water free from organic matter. In order to obtain water absolutely free from inorganic matter, the still-head should be provided with diaphragms which retain the particles of water and salt carried over by the steam. Distilled water has at first a special odour which it loses on standing in the air or on being filtered through wood-charcoal which has been previously heated to redness. It should leave no trace of residue on evaporation, should not become turbid with silver nitrate or lead acetate, and, in fact, should not give any chemical reaction which points to the presence of impurities. These tests are made on the water after it has been boiled to remove carbon dioxide which may have been absorbed from the air, and which reacts with silver and lead salts.

In the apparatus illustrated in Fig. 87, we see the boiler, *a*, which is filled to two-thirds of its capacity with hot water coming from the upper part of the receiver, *f*, through the cock *c*. The water is heated by indirect steam under pressure, which circulates in a coil terminating in a throttle-valve under the boiler. The steam which distils escapes through *e* and is made to follow a tortuous path before it arrives at the coil of the condenser, *f*. By this means the impurities and water-spray carried up by the boiling liquid are retained. The boiler is occasionally emptied through the lateral cock, so that no deposit may be formed.

The condenser water enters from the cock *b* below and escapes above where it is very hot from the tube *h*. The pure distilled water issues cold from the tube *g*. By means of a similar plant on a large scale as much as a thousand litres or more of distilled water are produced per day.

In chemical laboratories an apparatus similar to that illustrated in Fig. 88 is often used, in which steam from a water-bath is used which heats a steam oven with double walls for drying chemical preparations. The heat supply takes the form of an ordinary stove which is heated with gas, coal or wood.

NATURAL MINERAL WATERS. It is impossible to explain what may be called a mineral water at the present time. The current definition is debased by the influence of other than scientific factors. Commercialism, unscrupulous doctors, and complacent or interested chemists, all take part in the trade of the miracle-mongers and agree to deceive once more that larger part of the world which always consists of fools. In the past those waters were always called mineral waters which were not polluted and contained an excess of mineral salts (at least 1 grm. per litre); or which contained certain substances, such as arsenic, lithium, iodine, and CO_2, to which definite therapeutic effects were attributed. To-day waters are considered to be mineral waters when they contain only $\frac{1}{2}$ grm. per litre of mineral residue, and alchemistic traditions have been revived by attributing to these a definite and specific therapeutic action. If in the evaluation of mineral waters a rigorous system were to be followed, including positive and indisputable evidence of their medical effects, then very few of the innumerable waters of to-day would survive.

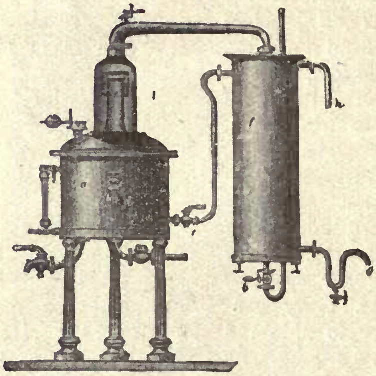


Fig. 87.

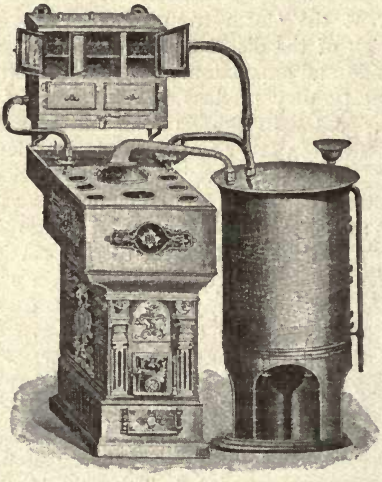


Fig. 88.

After these considerations we may say that the composition of the so-called natural mineral waters is very varied and that in many cases their temperature is very high.

Among the many possible classifications we may choose the following, not taking into account the factor of radio-activity which, however, appears to be present to a greater or less extent in almost all mineral waters, and the effects of which are still somewhat doubtful, although an explanation has thus been sought for the therapeutic efficacy of waters containing small amounts of salts.

We must remark that to-day it is believed to be possible to distinguish natural mineral waters from artificial imitations by means of their different electrical conductivity and of the radio-activity of some of them. Both factors can, however, be imparted artificially.

I. **Alkaline Mineral Waters.** These contain much soda and CO_2, and small proportions of alkaline earths, Na_2SO_4, and NaCl.[1]

---

[1] These are then divided into the following varieties:

(*a*) *Simple Acid Waters.*—These contain little solid residue and not less than 400 c.c. of CO_2 per litre (Heppingen, Apollinaris, Wernasser Springs, Sinneberger, Maria at Marienbad).

(*b*) *Acid-Alkaline.* These contain much Na_2CO_3 and CO_2 and little other salts (Vichy, Mont Dore, Neuenahr, Chaudes-Aigues, Biliu, Preblau, etc.).

(*c*) *Acid-Alkaline Muriatic.* These contain Na_2CO_3 and NaCl [Ems, Selters, Gleichenberg, Weilbach, Luhatzschowitz (iodine and bromine), Krankenheil, etc.].

II. **Glauber's Salt Waters** with much Na_2SO_4, together with Na_2CO_3 (Karlsbad, Bertrich, Marienbad, Salzbrunn, salt springs of Franzensbad, etc.).

III. **Chalybeate Waters.** These contain at least 0·06 grm. of iron salts per litre.[1]

IV. **Salt Water** containing much NaCl and other chlorides and small amounts of sulphates and carbonates.[2]

V. **Bitter Waters** containing $MgSO_4$ and Na_2SO_4. These are found at Pülna, Saidschütz, Sedlitz, Birmanstorf, Mülligen (Switzerland), Friedrichshall.

VI. **Sulphuretted Waters.** These contain sulphides and smell of H_2S: Stackelberg, Bagnères de Luchon, St. Sauven, Tabiano, Abano, etc.

VII. **Springs which are simply Hot: Thermal and Indifferent.** These contain little dissolved material but have elevated temperatures (above 24°). These temperatures are at Plombière, 19° to 65°; Tropuszko, 49° to 55°; Warmbrunn, 35° to 40°; Ragaz, 35°; Johannisbad, 29°; Wiesbaden, etc.

Certain mineral waters included in I. and VI. are also hot, for instance, those of Vichy, which have a temperature of 32·3°; Karlsbader Sprudel, 74°; Kochbrunner, 69°.

Some waters contain special metals, for example, that of Los Banctos in Chili contains 0·322 grm. of LiCl, and that of Salsomaggiore 0·735 grm. Certain waters contain bromine and iodine (*see* preceding Note). The water of Roncegno contains notable quantities of arsenic (0·124 grm. As_2O_5 per litre).

Other waters contain a large amount of silicates.

All these mineral waters are consumed to a great extent on the spot in delightful spas, which contribute more than a little to the therapeutic efficiency of the treatment, and a part is placed on the market in sterilised and well-closed bottles, and then forms those much-extolled table waters which are as much the subject of the play of fashion as are the large bonnets of the ladies!

A large trade in mineral waters, natural and artificial, is conducted in Italy and to a still greater extent in France and in Germany. In 1905, 9807 tons were imported by Germany of the value of £140,000 and 47,873 tons were exported of the value of £359,050. In 1904 Italy imported 2662 tons for £32,000 and exported 1700 tons for £16,700. In 1908 3304 tons were imported for £42,296 and 4231 tons exported for £40,620.

ARTIFICIAL MINERAL WATERS. These are imitations of the better natural mineral waters, but are distinguished from them by lack of radio-activity, and by their different electrical conductivity and cryoscopic behaviour (*see* p. 98). This, perhaps, also explains their different therapeutic value, but, as we have already said, these properties are now imparted artificially.[3] All types of mineral waters are manufactured on a very

---

[1] (*a*) *Pure Acid Chalybeate.* These contain few salts and much CO_2 [Schwalbach, Spa, Altwaser, Brückenau, Königwerth (Carolina spring at Marienbad), Frejenwalde, Recoaro, etc.]

(*b*) *Saline Alkaline Acid Chalybeate.* These contain $FeCO_3$ and Na_2CO_3, Na_2SO_4 and CO_2 in large amounts (Franzensbad, Elster, Cudowa, Flinsberg, etc.).

(*c*) *Saline Acid Chalybeate.* These contain $FeCO_3$, $CaCO_3$, and $CaSO_4$ (Pyrmont, Driburg, Griesbach, St. Moritz, Charlottenbrunn, Contrexéville, etc.).

(*d*) *Chalybeate Waters containing $FeSO_4$.* These are found at Alexisbad, Muskau, Mitterbad, and Ratzer in Tyrol, Parad in Hungary, etc.

[2] (*a*) *Simple Saline Waters with little NaCl* (Kissengen, Homburg, Kronthal, Neuhaus).

(*b*) *Saline Waters containing much NaCl.* These are found at Nauheim, Soden, Reichenhall, Wittekind, Sulza, Frankenhausen, and Hall near Innsbruck-Salzhausen.

(*c*) *Bromo-Iodo Saline Waters.* These contain much I and Br in the form of iodides and bromides of Na, K, Mg (Kreuznach, Elmen, Dürkheim, Hall in Austria, Salzbrunn, Wildegg, Bassen, Salice, Salsomaggiore, Abano, etc.). The bromo-iodo-saline water of Salsomaggiore is collected from artesian wells 700 metres deep. Its temperature is 14° and it has a density of 16° Bé. It contains 178·88 grms. of dry residue per litre consisting of 154 grms. NaCl, 0·735 LiCl, 0·637 NH_4Cl, 15·848 $CaCl_2$, 0·255 $SrCl_2$, 5·584 $MgCl_2$, 0·033 $FeCl_2$, 0·059 $AlCl_3$, 0·0057 $MnCl_2$, 0·304 $MgBr_2$, 0·066 MgI_2, 0·012 MgB_4O_7, 0·078 $Fe(HCO_3)_2$, 0·603 $SrSO_4$, 0·023 SiO_2 (Nasini and Anderlini, 1898); it is one of the richest waters in bromine and iodine in the world, and the richest in the world in strontium and lithium.

[3] The unit of measurement of the radio-activity of mineral waters was proposed by Mache in 1904. The quantity of emanation from 1 litre of the water was determined by passing through it a definite volume of air, in which an electroscope at a definite voltage was placed. The rapidity of decrease of the voltage during one hour was then determined. This diminution of voltage, after suitable corrections, was re-calculated into electrostatic units and then multiplied by 1000. If, for example, the quantity in electrostatic units corresponded with 0·000,000,000,33 amps., the unit proposed by Mache would be a thousand times smaller. The Fontactoscope is an apparatus which may be conveniently used for these determinations at the spring on the spot.

Artificial mineral waters are rendered radio-active by immersing an insoluble radium salt large scale, and apart from their therapeutic properties, a guarantee of the purity of the substances employed is necessary.

The manufacture of mineral waters was carried on as early as 1572, but the first factory on a scientific basis was founded in 1821 at Dresden by Struve, who recognised the importance of CO_2 for keeping in solution salts which would otherwise be less soluble or quite insoluble in water. The preservative action of CO_2 was known to him, and to-day the dissolved air is always expelled from the water in order that it may keep better. The pessimistic objections to artificial mineral waters have now disappeared, and when these are properly prepared the same effect can in many cases be produced as with a natural spring. After the year 1880 the manufacture of such waters underwent extraordinary developments by the application of liquid carbon dioxide, but even with artificial waters their success is often due merely to commercial speculation based on advertisement.

For the preparation of table water as a mere beverage, a good potable water suffices, with addition of a little sodium chloride or carbonate and subsequent saturation with carbon dioxide under pressure.

For the preparation of medical mineral waters it is necessary to employ pure distilled or sterilised water, which is mixed with the required salts and saturated with carbon dioxide at a pressure of 5 atmospheres. It is then placed in sterilised bottles with sterilised stoppers and kept at a pressure of 1½ to 2 atmospheres.

The carbon dioxide is prepared from magnesite or marble, and occasionally from bicarbonates, which are treated with commercial sulphuric acid; the gas is then washed with water, ferrous sulphate, sodium bicarbonate, and sometimes with permanganate solution (in order to remove odorous organic compounds).

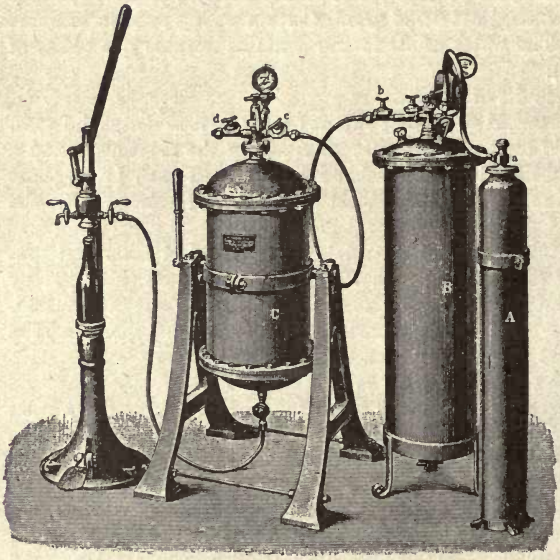


Fig. 89.

To-day, however, the use of liquid carbon dioxide has become general, as this is purer and more convenient, and is already under pressure (*see below,* Preparation of Liquid Carbon Dioxide).

A simple type of apparatus for the saturation of mineral waters or saline solutions with carbon dioxide is illustrated in Fig. 89. *A* is the cylinder of liquid carbon dioxide, and by means of the valve the expansion cylinder, *B*, is filled from this with gaseous CO_2, until a pressure of five atmospheres is indicated. The CO_2 is then passed through the cocks *b* and *c* into the mixed salts and water contained in *C*, which it saturates; the absorption is accelerated and increased by violently oscillating the vessel *C* or by the use of an internal stirrer actuated from without. If a pressure regulator is attached to the cylinder *A*, the expansion cylinder, *B*, may be dispensed with. In the figure we see how the mineral water is introduced into the bottles by means of a special cock which simultaneously drives in the stopper.

In many establishments sterilised water is employed instead of using ordinary drinking water.

(*e. g.*, the sulphate), enclosed in a cylinder of porous material, in them for a few instants, or use may be made of a product with a basis of the more soluble carbonate, enclosed in a semi-permeable mixture (Landin, 1914). The most active mineral waters are those of the ancient Roman fountain in the island of Ischia (30,800 units); those of Joachimstal in Bohemia, which show 14,000 units; of Baden-Baden, with 10,000 units; those prepared artificially for drinking purposes show 10,000 units, and those used for bathing purposes as much as 200,000 units.

Water saturated with compressed oxygen is also being gradually introduced at the present time.

ICE AND FREEZING MIXTURES

We have already studied the behaviour of water at low temperatures and have seen what happens during the separation of ice. Before speaking of natural and artificial ice, which is in general use for the production of low temperatures for varied industrial and hygienic purposes, we shall say a few words on artificial methods of producing cold.

FREEZING MIXTURES. These are ordinarily formed of salts or of saline mixtures which on dissolving in water produce considerable lowering of temperature. This depression of temperature generally becomes greater with increase of the following factors: the heat of solution (that is, the heat required to dissolve the salt), the solubility of the salt, the concentration of the resulting solution, and therefore also the lowness of the freezing-point of the latter; the limit of maximum refrigeration is given by the freezing-point of the saturated solution.

Mixtures of salts produce greater temperature depressions than simple salts, because they dissolve in less water and therefore give more concentrated solutions. The saline mixtures should be well powdered, and the ice should be well pounded in order to obtain the maximum cooling effect.

With a mixture of 5 parts of HCl and 8 parts of Glauber's salt (crystallised sodium sulphate) a lowering of the temperature by 28° may be obtained. With 1 part of sodium chloride and 3 parts of powdered ice or of snow, a refrigeration of 21° is obtained (if in this case the initial temperature is 0° a temperature of — 21° may be obtained). With 5 parts of ammonium nitrate, 1 part of ammonium chloride, and 3 parts of water, the temperature is lowered by 30°. On mixing crystallised calcium chloride (not the fused substance) with water, the temperature is lowered by 48·5°. With 3 parts of ammonium chloride, 2 parts of potassium nitrate, and 10 parts of water, the temperature is lowered by 26°. If to this last mixture 4 parts of Glauber's salt are added, the diminution of temperature amounts to 32°. With 15 parts of potassium thiocyanate and 10 parts of water a temperature depression of 34° is obtained.

Freezing mixtures are employed to a limited extent only in laboratories and in certain small special industries. For large industrial operations natural ice, or more especially artificial ice and large freezing machines, are now used. Since 1870 these have been greatly improved, so that they have to-day reached a high degree of perfection.

The theoretical explanation of the behaviour of freezing mixtures is given by the following considerations: when a salt is dissolved in water—apart from the phenomenon of ionic dissociation (which occurs in dilute solutions, whilst we have to do with concentrated solutions)—the lowering of the freezing-point of the solvent is the greater the more salt has been dissolved (cryoscopy). The maximum lowering of the freezing-point corresponds with the freezing-point of the solid solution, which is merely the multiple point (*see* phase rule, p. 120) of a system in complete equilibrium, and in this case it is also called the *cryohydric* or *eutectic* point.

Furthermore, on dissolving, the salt produces a cooling effect which is the greater, the greater its heat of solution. This rule is a deduction from Le Chatelier's principle (p. 64) or more exactly from the principle of mobile equilibrium enunciated and mathematically demonstrated by van't Hoff in order to explain many important phenomena.

This principle states that any displacement of the factors regulating a system in equilibrium produces transformations in the system which counteract the action of the modified factor.

In accordance with this rule of antithesis, salts which dissolve in the cold with development of heat are either less soluble or but little more soluble in the hot, for example, sodium chloride, calcium hydroxide, calcium sulphate, and sodium sulphate; on the other hand, bodies which dissolve in the cold with absorption of heat, for example, potassium nitrate, are more soluble hot than cold, and the solubility is the greater as the absorption of heat is greater. Consequently the amount of cold produced when a salt is dissolved in water is greater as its solubility is greater. The intimate connection between solubility and heat of solution is thus evident.

The heat of solution in these cases is given by the rise of temperature necessary in order to dissolve a further quantity of salt in a saturated solution. In fact, when we have a system formed of a saturated solution in presence of an excess of solid salt, on lowering the temperature a certain quantity of salt ordinarily separates, and in order to be able to dissolve a further quantity, the same quantity of heat is necessary which had been first removed. Thus the more the amount of salt dissolving in a solution, the greater will be the absorption of heat.

If we add ice to a system formed of a solid salt and its saturated solution at 0°, the system is no longer in complete equilibrium, because the freezing-point of the solution saturated at 0° (cryohydric point) is much lower, and in order to reach it the temperature must be depressed. This is possible if the ice melts, because on melting it absorbs heat (80 Cals. per kilo). Thus if ice and salt are present in sufficient quantities to maintain the solution in a state of saturation, then as the ice melts it will gradually continue to lower the temperature until the freezing-point of the saturated solution (cryohydric point) is reached. Complete equilibrium is there attained, and only then are the ice and salt able to co-exist.

ICE, the properties of which we have already studied on pp. 224 *et seq.*, is employed in breweries, spirit distilleries, paraffin works, margarine factories, chocolate works, coal-tar colour works, dyeworks, dairies, cheese factories, sugar refineries, tobacco, glue and gelatine and perfume factories, in the mercerisation of cotton, in the rubber industry, in the preparation of Glauber's salt from $MgSO_4$ and NaCl solutions, and generally for many crystallisations. It is also much used on vessels and railway wagons carrying carcasses and foodstuffs in general. Refrigerating chambers are to-day also used for the preservation of dead poultry and eggs (*see* Vol. II., "Organic Chemistry").[1]

Thus the industrial use of ice on a large scale has developed in an extraordinary manner during the last few years. Ice which is to come into contact with foodstuffs or beverages should correspond with all the requirements of a potable water.

NATURAL ICE. During their mild winters southern countries import large quantities of natural ice from more northern climates. In North America especially a regular industry of this kind exists with suitable and perfected machinery for obtaining natural ice, especially from the frozen lakes.

By means of a kind of planing machine, about 2½ cms. of the surface, which is impure,

---

[1] The conditions to be observed in refrigerating chambers vary with the nature of the substances to be preserved. With eggs the temperature should not fall to 0° or exceed 3–4° and the degree of humidity should be 70–80, so that the water holding the egg-white in solution may not evaporate appreciably. Eggs are very sensitive to smells and fix them tenaciously, so that the eggs to be preserved should be clean and free from straw, while the air of the chamber may, if necessary, be deodorised by means of small quantities (less than 0·3 mgrm. per cu. metre) of ozone.

Beef and mutton for ocean transport are completely frozen at a temperature a few degrees below zero and are kept frozen on board ship. Before consumption the meat should be thawed gradually in suitable chambers, slowly rising in temperature until the ordinary temperature is almost reached, since otherwise the atmospheric moisture charged with micro-organisms is deposited on it. Such thawed meat should be consumed as soon as possible as it undergoes alteration more easily than non-frozen meat in which the cellular protoplasm is still living. Fresh meat is often kept in the summer at a temperature between 0° and 5°; in this case the degree of humidity should be 80–85 and the air should be renewed gradually by means of a fan, being drawn from the outside through the cooling tubes and moistened before it enters the cold chamber. Plucked fowls should be kept frozen below 0°; capons, drawn and without head and claws, are coated with a layer of ice (10–15 mm.) by cooling them to − 5° or − 6°, and then immersing them in water at almost 0°, and are then kept at − 2° to − 3°. As the result of many experiments, Pennington (1914) showed that to keep game best, it should not be drawn and should be left with the feet and head.

Refrigerating chambers are used by florists to prevent plants from blooming during the normal season; flowering and fructification occur later with great vigour, the fruit and flowers thus obtained out of season commanding high prices.

is removed; a traction-engine is then employed, which carries several circular saws on an axis, and these saw through the mass in directions at right angles, to form large blocks of ice containing individual subdivisions which still adhere slightly (about 100 subdivisions to each block). Large cubes are thus separated which can be broken up with chisels and carried to the coast for transportation to South America and even to Australia.

Similar but smaller plants are not rare in Europe, and in former times were fairly widespread. That of the Norddeutsche Ice Works in Berlin produced 30,000 tons of ice in the winter of 1871.

Norway supplies large quantities of ice, which are quarried from its glaciers by working them much in the same manner as a mine. This is exported to England in large quantities at a price varying from 2*s.* to 2*s.* 6*d.* per ton at the port of shipment. In 1901 346,000 tons were exported, and in 1902 285,000 tons.

In France more than one million tons of ice are consumed annually, of which the bulk is natural (850,000 tons), 60,000 tons of which are imported from Norway to the value of more than £40,000 at their destination.

Ice was at one time stored in underground cellars or ice-houses, which were costly and inconvenient. Nowadays ice-houses are built above ground with double wooden walls between which insulating material, such as sawdust, peat, or, still better, rice husks, is placed.[1] Double walls of masonry also suffice, and in that case the insulating layer is formed of air. The doors are double, with a northern aspect, and the ice rests on a perforated false floor so that it may not be in contact with the water produced on melting, which, if not separated and removed by a syphon tube, would accelerate the melting of the ice. All access of air from outside is avoided as far as possible in order to preserve the ice, because the external air is always warmer than that inside the ice-house.

ARTIFICIAL ICE. Machines for the production of ice or artificial cold are based on the absorption of heat which occurs on rapid evaporation of a cold and easily volatile liquid, for example, ether boiling at 35°, ammonia at − 33·5°, sulphur dioxide at − 8°, carbon dioxide at − 78°, and even water (Carré's machine).

Another type of machine, on the other hand, is based on the cooling effect produced by a strongly compressed gas (for instance, air) when this is allowed to expand rapidly.

The boiling-point of a liquid is raised when the latter is exposed to pressure, and is lowered when the pressure is diminished. In some ice machines the heat of evaporation is abstracted from the evaporating liquid itself by preventing access of heat from without, and the liquid then becomes the colder the less the pressure and the lower its boiling-point, because a small reduction of the pressure then causes great evaporation of the liquid. The reason why intense cooling is produced by liquid carbon dioxide is thus explained because this boils at a very low temperature. Ammonia, methyl chloride, methyl ether, and sulphur dioxide follow in order of efficiency (*see* p. 226, Heat of Evaporation).[2]

---

[1] Felt is the best insulator, and if its value be taken as 100, that of wool will be 80, sawdust 70, clay and cork 50, asbestos 40, ashes 35, and fine coke 30. The brick walls of the refrigerating chambers, the brick roof, lined internally with cement, and the cement floor should be insulated from the external air and from the ground with layers of insulating materials (often thick plates of agglomerated cork are used) 10–20 cm. thick. Walls not insulated in this way lose about 1½ cals. per sq. metre per hour per degree of temperature difference between the inside and outside, while the corresponding loss with a well-insulated wall is 0·8–0·3 cal. It is, therefore, a mistake to economise in insulating material, since a loss of 1500 cals. corresponds with about 1 h.p., and in some cases badly insulated plant requires double as much power as one well insulated giving the same cooling effect.

[2] *The Theory of the Ice Machine.*—The refrigerating power of a machine is given practically by the number of *frigories* which it produces per hour, that is, by the number of calories which it abstracts from the bodies to be cooled. The *frigorie* is merely a negative calorie. The yield of the freezing machine is expressed by the relation between the work which it consumes and the heat abstracted from the substances to be cooled. For a perfectly reversible machine, working between the temperature limits T_1 and T_2, the yield is the greater the smaller the difference between these limiting temperatures. For the production of ice it would therefore be best

The *chemical analysis of ice* is carried out as with water, but one need not consider the ammonia which may have been absorbed from the atmosphere of the works.

Ice machines using ammonia. In actual practice ice machines make use either of ammonia, of liquid sulphur dioxide, or of liquid carbon dioxide. The machines which are most used are those of Linde using ammonia, which are constructed of the following parts, represented diagrammatically in Fig. 90. The compressor, *C*, is a pump with inlet valves, *Va*, and outlet valves, *Vp*. The necessary quantity of ammonia is first introduced into the machine by temporarily uniting the valve *Va* with a bomb of pure liquid ammonia free from water, such as is placed on the market by various manufacturers. The gasified ammonia is gradually compressed by the compressor, *C*, into the tube *T*, which terminates in a very long coil surrounded by water circulating continuously in the tank, *D*, called the condenser, in order to cool the ammonia which is heated by the compression. In this way liquid ammonia accumulates in the lower part of the coil

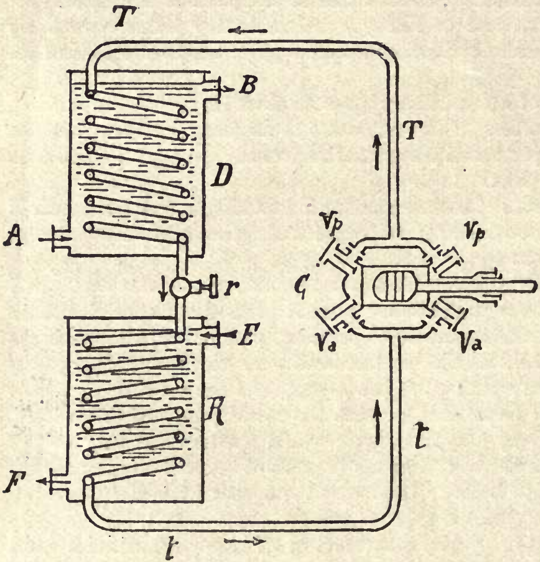


FIG. 90.

---

if the lower limiting temperature were not much inferior to 0°, apart from the mechanical difficulties of an easy interchange of heat between the water to be frozen and the brine which circulates in the apparatus. The quantity of heat, Q_o (in Calories), to be abstracted from a kilo of water at $+ t°$ in order to transform it into 1 kilo of ice at $- t_1°$ is given by the formula : $Q_o = (79 + t + ct_1)$, where 79 is the heat of fusion of ice, or the amount which must be absorbed from the water in order to freeze it, and c is the specific heat of ice. Thus, starting from water at + 17° in order to obtain ice at − 8° : $Q_o = 79 + 17 + (8 \times 0{\cdot}5) = 100$ Calories. We must also take into account the interchange of heat between the surrounding atmosphere and the whole of the machinery; this may be calculated for each machine and is proportional to the rise of temperature, $T_2 - T_1$; finally, we must take into account the practical yield, which is smaller to a more or less extent than the theoretical yield according to the perfection of the machinery and to the insulation and size of the machine. Machines of very large capacity give the highest efficiencies.

An ice machine with a capacity of 12,500 negative Calories (frigories) per hour, *i. e.*, 300,000 per 24 hours, gives about 100 kilos of ice per hour (1 kilo per 125 frigories), or 24 quintals per 24 hours. If such a machine is used solely for cooling a refrigerating chamber, 10 × 5 × 4 metres, with external and internal temperatures of 30° and − 10° respectively, a loss of about 0·6 Cal. per hour per degree of temperature difference per sq. metre through the wall, 0·8 Cal. for the floor (taking the temperature of the ground to be 15°), 0·4 Cal. for the ceiling, and 2 Cals. for the double door and window may be assumed. Thus the losses are :

For the 4 lateral walls, $(10 + 10 + 5 + 5) \times 4 \times 40 \times 0{\cdot}6$	= 2880 Cals.
,, floor, $(10 \times 5) \times 25 \times 0{\cdot}8$	= 1000 ,,
,, roof, $(10 \times 5) \times 40 \times 0{\cdot}4$	= 800 ,,
,, door and windows, $4 \times 40 \times 2$	= 320 ,,
Various losses (during charging and discharging, etc.)	= 1080 ,,
Total loss per hour . . .	= 6080 ,,

Further, 200 cu. metres or 260 kilos of air with a sp. heat 0·2377 and for a temperature difference of 40° (assuming the air to be changed once every 24 hours) will consume :

$$260 \times 0{\cdot}2377 \times 40 \div 24 = 103 \text{ Cals.},$$

so that 6180 Cals. will be required per hour to maintain the chamber at − 10°. The residual 6320 (12,500 − 6180) Cals. may be used for the production of ice (6320 ÷ 125 = 50 kilos per hour).

The first refrigerating machines (about 1873) showed a thermodynamic efficiency of 25 per cent., which was subsequently increased to over 50 per cent. by utilisation of the expansion of liquefied and compressed gases or vapours and by mechanical improvements. A further advantage attends the direct use of the cold without preparation of ice, the cooled brine from the machine being circulated.

of the condenser and is gradually allowed to enter through the cock *r* into the refrigerating coil, *R*, which is in connection with the inlet valve, *Va*, of the compressor, *C*, by means of the tube *t*. The compressed liquid ammonia instantly evaporates on entering *R* under the exhausting action of the pump, producing considerable cold. The coils of *R* are surrounded by brine (concentrated solution of magnesium or calcium chloride) which becomes strongly cooled and serves to freeze water contained in suitable moulds of sheet iron, which are immersed in this very cold solution. Work may naturally be continued for a long time with the same quantity of ammonia, because this is exhausted from *R* at the same time as it is compressed in *D*. Fig. 91 shows the freezing machine of Linde as it is used in many factories. The compressor is worked from a large flywheel. Vertical agitators worked by cog-wheels are used in the condenser and refrigerator, so that the temperature of the coils may be rapidly communicated to the liquids. The coils consist of very close spirals and are made of iron in a single piece without any seam, in such a way as to resist high pressure. There are few works in Europe which construct them satisfactorily. In the condenser ordinary water circulates at a temperature of 10° to 20°, and in the refrigerator use is made of a 30 per cent. aqueous solution of calcium chloride, which does not freeze even at 12° below zero.

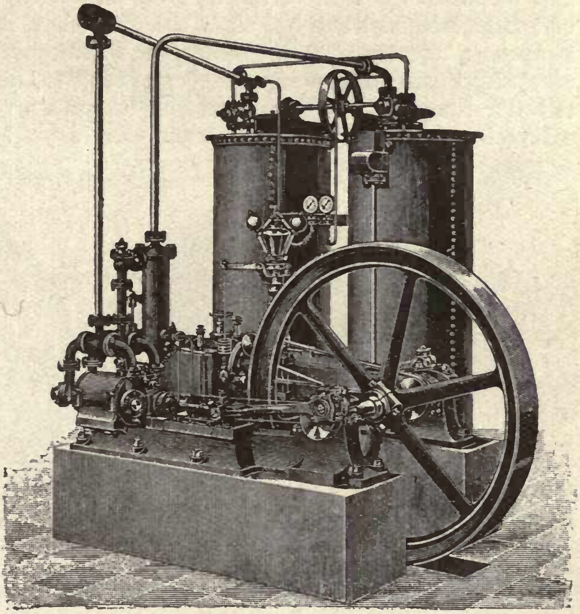


FIG. 91.

This brine is cooled by the ammonia which evaporates in the refrigerating coil and is pumped into a tank at the side, called the freezing-tank, which should not be far from the machine and is not shown in the figure. In this tank are placed the sheet-iron boxes or moulds containing the drinking water to be frozen. The brine circulates continuously between the freezing-tank and the refrigerator.

A light rod moves automatically in the middle of each box containing the water, in order to facilitate the escape of the dissolved air, so that transparent ice may be obtained; otherwise the small air-bubbles render the ice opaque. These rods are removed a few moments before the water in the centre of the box is frozen. The impurities in the water collect in the centre of the ice-block, because this is the portion to be frozen last.

Large plants contain automatic contrivances which lift out and remove ten boxes at once when the ice-blocks are completely formed, and refill the boxes with fresh water.

These Linde machines are constructed in all sizes for the production of from 50 kilos to 2000 kilos of ice per hour.[1] During the last twenty-five years more than 6000 Linde

---

[1] The cost of a Linde machine, including erection—exclusive, however, of the motor—would be approximately as follows:

					£
For the production of	100	kilos per hour	with	6 h.p.	600
,, ,,	500	,,	,,	20 ,, ...	1600
,, ,,	1000	,,	,,	40 ,, ...	2920
,, ,,	2000	,,	,,	65 ,, ...	4400

From plants producing 5 tons per day the ice costs about 8*s.* per ton.
,, ,, 40 ,, ,, ,, 3*s.* 3*d.* per ton.

In ice factories employing machines working with ammonia, safety apparatus should be provided in case of escape of ammonia or of explosion. Safety-masks and respiratory apparatus are machines have been constructed, 46 per cent. of this number having been supplied to breweries.

If instead of producing ice it is desired to cool rooms, etc., the brine is circulated in numerous winged tubes such as are employed for heating (*see* Note, p. 261, and Fig. 94).

Freezing machines using dry air. The first to propose the utilisation of the expansion of compressed gases for the production of cold was Herschel in the first half of the nineteenth century. In 1852 Smyth and Nesmond constructed the first machine which utilised this principle for producing ice. It was improved in 1862 by Kirk, but it only became practicable through the work of Windhausen in 1869. He improved it still further, and to-day it is constructed in very large sizes, and serves especially for the refrigeration of large air spaces and food stores.

Later on, in the chapter on Liquid Air, we shall discuss the calculations and formulæ which show the amount of cooling produced by the expansion of compressed air, and we shall then see that the reduction of temperature is about a quarter of a degree for each atmosphere resulting from the difference of pressure before and after expansion. This datum is of practical value only for temperatures near zero, and for pressures which are not very large, whilst for temperatures much lower than zero the cooling is much less than a quarter of a degree per atmosphere.

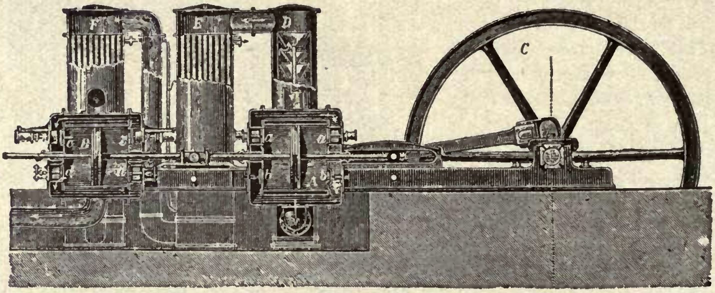


FIG. 92.

We may here explain the principles on which the refrigerating machines of Windhausen which use air are based. One of the most largely used types of this machine is reproduced in Fig. 92. The cylinder *A* is the compressor and *B* the exhauster. The pistons of both cylinders are connected with a common piston-rod moved by a flywheel, *C*. The air enters through the valves *a*, which open inwards alternately in accordance with the movements of the piston. The strongly compressed air escapes alternately by the valves *b*, which open only when a certain pressure is reached. The air thus compressed issues through a wide tube and then rises into a cylinder, *D*, containing several funnels of sheet metal, which serve to cool it, and to condense the moisture which it contains, so that it arrives fairly dry in the exhauster *B* by means of the valves *c*, after having traversed the groups of pipes contained in the cylinders *E* and *F*, through which a continuous current of cold water circulates. The water circulates in an opposite direction to the air, entering at the lower part of the cylinder *F*, passing out from the upper part of this cylinder, descending to the base of the cylinder *E*, and passing out from the upper part. The air entering the cylinder *B* overcomes a certain weight on the valve *e*, which opens towards the interior, then expands and becomes strongly cooled (even down to — 40°), and issues through the valve *d*, whence it is conducted into the places where the cooling is to be

---

required for the workmen who may have to be employed for rescue or repairing operations. Explosions have sometimes occurred which have been explained by excessive compression (up to 40 atmospheres), which produces so much heating as to cause, under certain conditions, a partial decomposition of the ammonia into H_3 and N, thus doubling the volume. If a flame is present in localities in which this occurs, explosions may be caused by the ignition of the detonating mixture of hydrogen and air.

effected, or into the boxes where ice is made. In the latter case it may be recovered in order to be brought back into circulation, as it is always dry and already considerably cooled.

Machines using sulphur dioxide are the best as regards efficiency, but are very large and cumbersome, being sixteen (or even more) times as large as carbon dioxide machines.

Various other types of ice machine exist, *e.g.*, that of Pictet, in which use is made of a special liquid consisting of a mixture of liquid sulphur and carbon dioxides boiling at — 19°. These machines were formerly used in France, but nowadays there are very few of them.

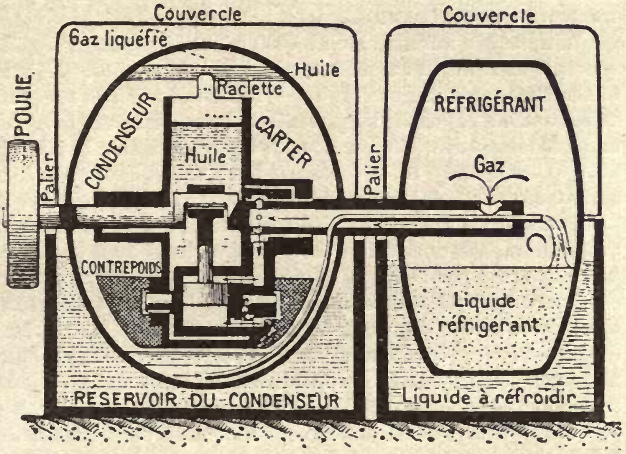


FIG. 93.

During recent years increasing use has been made of the small Audriffen-Singrün ice or cooling machine in which liquid sulphur dioxide is used. This is a very ingenious contrivance and works continuously and automatically without supervision. As seen from Fig. 93, it consists of two almost spherical, completely enclosed parts (the condenser, *C*, and the cooler, *R*), which communicate by means of a hollow spindle, which is worked by an external pulley, *P*, and on which are fixed both the condenser and cooler, these rotating with the spindle. Inside the condenser is mounted a small compressor, of which the piston with a loose rod is moved by the revolving axle, at this point curved like a goose neck. The whole compressor is carried by the axle without being rigidly fixed to it, being supported by bearings immersed in perfectly neutral mineral oil. The compressor is kept below and vertical—even when the spindle rotates—by means of a heavy counterweight surrounding it. When the piston is working, it draws vapour from the liquid sulphur dioxide in the revolving cooler—which dips into the brine—and thus causes cooling, the compressed vapour expanding and liquefying against the inner surface of the condenser (which rotates and is surrounded outside to one-half its height in cold water). The liquid sulphur dioxide thus regenerated separates in virtue of its density from the lubricating oil and returns to the cooler through a tube which reaches to the periphery of the condenser, *C* (and rotates with this), and empties at the end of the spindle in the cooler, *R*, where the aspiration occurs. The oil separated passes, by means of a scraper which collects it, to the interior of the capsule, this closing the compressor quite drowned in the oil.

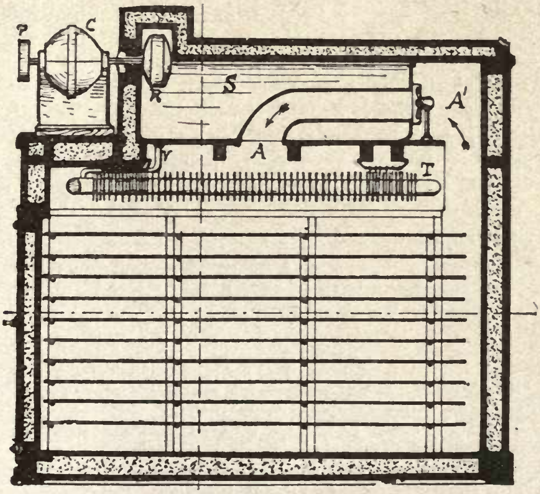


FIG. 94.

If moulds containing water are placed in the brine, the water is frozen. If, however, as in the refrigerating chamber shown in Fig. 94, the brine, *S*, raised by adhesion by the rotating drum of the cooler, *R*, is caused to circulate in the vaned coil and to return by displacement into the base of the brine vessel through the tube *V*, the air in the chamber may be cooled as desired—to −10° or −12° (*see* examples and calculations in the Note on p. 259). The air in the chamber, *A*, circulates spontaneously in the sense of the arrows and passes over the vaned coil, where it is cooled, then falling and displacing less cold and less dense air, which rises towards *A′*; this circulation may be rendered more efficient by means of a small fan at *A′*.

With such a machine giving 6600 frigories per hour, a cold chamber having a utilisable contents of 10 to 12 cu. metres may be kept at − 8°. This machine, which is the largest of the type, produces cooling to − 10° if the water is at + 10° on entering the condenser vessel and at 24° on leaving, besides giving 50 kilos of ice per hour; 3 h.p. are required and 1400 litres of water per hour in the condenser. If this quantity of water is not available, as little as 16 to 18 litres per hour will suffice, provided that air is blown on to the surface of the revolving condenser by means of a ½-h.p. fan so as to cause rapid evaporation of the water on the sphere of the condenser; since 1 litre of water requires 534 Cals. for evaporation, the removal of 6600 Cals. requires 6600 ÷ 534 = about 13 litres of water to be evaporated per hour.

Compared with others of similar capacity, this apparatus saves about 50 per cent. of the power, and if the water-economiser is used (*i. e.*, the fan), 90 per cent. less water is consumed for the condenser. Further, all those mechanical contrivances which in ordinary machines require constant supervision (pumps, cranks, joints, stuffing-box, manometers, cocks, and especially the exhauster tube, which is easily obstructed) are dispensed with. It works without attention, except that once or twice per day the two bearings require lubricating.

Machines using carbon dioxide. These are widely used, as might be supposed according to the theoretical advantages which they possess over those using ammonia. CO_2 does not attack the metallic portions of the machine; it is less poisonous and dangerous than ammonia in case of gas escape. However, such leakages, whilst they are easily noticed by means of the odour in the case of ammonia, are not so easy to detect in machines using CO_2.

In order to obtain an equal refrigerating effect, machines using CO_2 theoretically require a space six times smaller than those using NH_3, and sixteen times smaller than those using sulphur dioxide, so that smaller and less costly machinery should be required. Practically, however, it is not possible to reduce the proportions of machinery to these limiting values. During the last few years the compressors have been greatly improved, and these machines to-day tend to replace those mentioned above. A machine with a capacity of 15,000 frigories per hour is charged with about 100 kilos of liquid CO_2.

USES OF ICE. The refrigerating industry has to-day acquired an extraordinary importance, and numerous industries are connected with it (*see* p. 258).[1]

Through the use of refrigerating machines on board ship, England was able to import in 1900 the following products from far distant regions: 6,434,000 frozen sheep from

---

[1] An important application of cold and hence of ice machines is for the drying of air and of gases generally; hygroscopic substances (conc. sulphuric acid, fused calcium chloride, quicklime, etc.) are not capable of drying the large quantities of air now required in many industries (*e. g.*, blast furnaces, drying plant, refrigerating chambers, etc.). The vapour-pressure table for water (p. 224) and that giving the moisture contents of air saturated with moisture at different temperatures (*see* Table, p. 337), show how it is that depression of the temperature of a space saturated with water vapour results in a precipitation in the liquid state of part of the water present. If the sulphuric acid of a desiccator is replaced by ice (which has a very small vapour pressure) moisture will condense on the ice from the moist object (which has a greater vapour pressure). Only at the freezing point is it possible for water, water vapour and ice to co-exist (*see* phase rule, p. 118). Supercooled water, *i. e.*, liquid below 0°, has a vapour pressure greater than that of ice at the same temperature, and if a piece of ice is thrown into it, the whole of the liquid water is converted into ice, that is, it distils on to the ice which rapidly forms. The difference in vapour pressure between supercooled water and ice increases as the temperature is lowered, and at −10° the value for such water is 1½ times that for ice, at − 40° twice, at −100° three times, and at −170° thirteen times; hence, the lower the temperature of the ice, the greater is its drying power. Thus, when moist air is passed over ice or over objects at a temperature below 0°, the moisture is condensed or precipitated as ice on the cold bodies.

Australia, New Zealand, and South America;[1] 60,000 tons of frozen and refrigerated beef from America and Australia; 65,900 tons of butter from Australia, New Zealand, the United States, and Canada; 167,000,000 eggs from Morocco, Egypt, United States, and Russia; and to these must be added enormous quantities of fresh fruit, salmon, game, etc. The total value of these important products for 1900 was £26,600,000; in 1907 it rose to £36,000,000. In 1909 England consumed altogether 13,451,484 tons of beef and 649,000 tons of mutton, one-third of this amount being brought frozen from the Argentine by means of a service of 200 steamers and kept in 28 cold stores. In London frozen meat costs about 3*d.* less per kilo than cold-stored, and the latter 3*d.* less than fresh meat. England first imported cold-stored meat in 1900.

In 1909 France possessed 400 ice machines and the United States 2500 with a capacity of 2600 tons of ice per hour, while the total capacity in Germany amounts to 650 tons per hour.

Of 850 slaughter-houses in Germany, 350 possess complete refrigerating plants. In the United States in 1910 there were 90,000 refrigerator vans, in Russia about 1000, and in France a few hundred.

Frozen meat loses 4–5 per cent. of its weight in 30–50 days and cold-stored meat more than 10 per cent. in 50 days.

The mean annual consumption of fresh meat in Italy is 18 kilos per head (74 kilos in Milan, 49 in Florence, 40 in Rome, 22 in Naples, 16 in Palermo, and 4 in Trapani); in France the amount is 35 kilos, in Germany 46, in England 51, in Denmark 52, and in the Argentine and Australia, 110.

In the United States 12,000,000,000 tons of foodstuffs are preserved by cold each year. The preservation and transportation of fruit are often carried out by freezing it to — 4° during transport and in the warehouses before consumption.

The English companies pay £3 8*s.* per ton for the transport of frozen meat from Buenos Aires to London, whilst the transport to Genoa costs £8 16*s.* per ton.

Until a few years ago only three public slaughter-houses in France were provided with refrigerating machinery. In France in 1902–1903 there were 1077 ice machines, of which 55 per cent. were worked with ammonia, 27·8 per cent. with sulphur dioxide, 11 per cent. with carbon dioxide, and 7·6 per cent. with methyl chloride. In 1912 France possessed 360 refrigerator vans with ice and 25 with freezing machines.

During the very hot weather experienced in August 1911, more than 4000 tons of ice were consumed per day in Paris.

In the United States 4,500,000 tons of artificial ice are produced annually, together with 20,000,000 tons of natural ice. The capital represented by the freezing machinery, ice factories, and cold stores in the United States in 1913 amounted to £12,000,000.

In 1912 New Zealand exported fully 5,656,000 head of slaughtered cattle, mostly calves and sheep, of which the various offals and the flesh are utilised or preserved cold separately; in order that they may not undergo change, they are heated rapidly to 70° and then cooled immediately. The intestines are washed well and salted, while the head, lungs, liver, etc., are boiled to extract fat for exportation; the dried coagulated blood is added to the meat meal (good cattle food) obtained from the detritus of dried and powdered meat.

A large brewery in St. Louis produced in 1913 about 160 tons of ice daily, while a single New York ice company made 400 tons per day. In 1913 eight Chicago ice factories, with a central electric plant, produced together 150,000 tons of ice. In 1912 the city of New York consumed about 5,000,000 tons of ice (1 ton per inhabitant). In the United States there are 20,000 refrigerating machines and 3500 ice factories with an output of 13,000,000

---

[1] In 1909 there were 29,116,625 oxen and 67,211,854 sheep in the Argentine. Refrigerated meat arriving in England is kept for not longer than 3–4 weeks, whereas frozen meat keeps indefinitely, but acquires a peculiar taste after 3–4 weeks. Before consumption meat to be cold-stored is kept for three days at a few degrees above 0°, and then at 1–2° below 0°; meat to be frozen is kept in cold store for some days and then brought to 7–10° below zero. Cold storage vessels carry up to 5000 tons of meat, a specimen cargo containing: 8000 hind-quarters of beef, 12,000 fore-quarters, 24,000 sheep, 7400 lambs, 21,500 sides of beef, 13,000 ox tongues, 27,800 sheeps' hearts, 4800 pieces of meat, 28,750 sheeps' kidneys, and 8950 ox-livers, of a total weight of 2600 tons. The passage from the Argentine to London lasts about twenty-five days and the freight amounts to about £3 4*s.* per ton. Transport in refrigerator vans in England for a twelve hours' journey costs less than 32*s.* per ton, each van holding about five tons.

tons of ice. The German artificial organic dye factories have refrigerating plants with a capacity of 2000 tons of ice per day.

HYDROGEN PEROXIDE: H_2O_2

This substance was first produced by Thénard in 1818 by the action of HCl on barium peroxide.

It is formed in the atmosphere by powerful electrical discharges or heavy snowfalls. Snow may contain as much as 1 mgrm. of hydrogen peroxide per kilo.

It is formed in very small quantities during the combustion of hydrogen and hydrocarbons. It is also produced wherever ozone is found in the presence of water; also on burning hydrogen in air, and thus also during the slow combustion of ether. A hot platinum spiral becomes red hot in contact with ether vapour and then forms H_2O_2. Some metals (Cu, Fe, Pb) form a little H_2O_2 when agitated with H_2SO_4 and air.

PROPERTIES. Pure concentrated hydrogen peroxide decomposes easily into $H_2O + O$, developing heat (97 Kj = 23,180 cals.), and decomposes with a powerful explosion if it contains impurities. Sometimes a violent shock or even contact with dust in the air and with impurities is sufficient to cause its decomposition and explosion, so that it is not wise to store pure hydrogen peroxide (*see below*). Pure and free from water, it is a colourless, syrupy liquid boiling at 84–85° under 68 mm. pressure, or at 69·2° under 26 mm. pressure; its sp. gr. is 1·5 at 10°.

H_2O_2 is an energetic oxidising agent and decolorises dyestuffs, liberates iodine from iodides, and transforms sulphurous into sulphuric acid, and sulphides into sulphates. It also transforms oxides of Ca, Ba, and Sr into the peroxides. With H_2S it separates sulphur and forms H_2O.

Some very finely powdered metals (Au, Pt, Ag, etc.) evolve oxygen in contact with H_2O_2 without alteration of the metal itself. Manganese dioxide, MnO_2, is reduced in presence of an acid and of H_2O_2, liberating half its own oxygen together with one atom of oxygen from the H_2O_2. Certain rather unstable metallic oxides (of Ag, Au, and Pt) are also reduced with evolution of their own oxygen united to that liberated by the H_2O_2. In a similar manner potassium permanganate is reduced to manganous oxide, which forms manganous sulphate in presence of H_2SO_4 with decolorisation of the permanganate and evolution of oxygen. With chromic acid chromium oxide is obtained. H_2O_2 reacts with sodium hypochlorite, producing water, oxygen, and sodium chloride. Thus we see that hydrogen peroxide is also able to effect energetic reductions owing to the avidity with which the atomic oxygen of the hydrogen peroxide combines, when liberated, with another atom of oxygen of an oxygenated substance, thus being transformed into the more stable molecular oxygen, O_2.

The size of the molecule of hydrogen peroxide has been measured by cryoscopic determinations. In an electrolytic cell, H_2O_2 is decomposed at both the anode and cathode.

CHARACTERISTIC REACTIONS OF H_2O_2. Hydrogen peroxide decolorises indigo solution alone, and still more rapidly in presence of a little ferrous sulphate. With starch paste and potassium iodide a blue coloration is obtained owing to the liberation of iodine, and this reaction is also more sensitive in presence of a trace of ferrous sulphate.

A fairly sensitive reaction is as follows: 1 c.c. of a 1 per cent. solution of cobalt chloride ($CoCl_2 + 6H_2O$) is mixed in a test-tube with 1 c.c. of a solution composed of 1·6 parts of borax, 20 parts of glycerine and 100 of water, and the liquid to be tested is poured on to the top of the mixture. A brown coloration forms after a few moments at the surface between the two liquids and then gradually diffuses. Perborates also give this reaction, whilst persulphates give it only in presence of alcohol and after some time (Leuchter, 1911).

The following is a very sensitive reaction: solutions of ferric chloride and potassium ferricyanide (red prussiate) are mixed, and a very small quantity of hydrogen peroxide is then added. The ferricyanide is reduced to potassium ferrocyanide, which immediately forms Prussian blue with the ferric chloride. With very minute traces of hydrogen peroxide the coloration is green.

A colourless solution of titanium dioxide in concentrated sulphuric acid is coloured orange-yellow by minimal traces of H_2O_2, through the formation of titanium peroxide. (*Translator's note.*—The original text says titanic anhydride, which is obviously a slip.) Vanadium salts give a similar reaction.

The reaction with benzidine, which we have already described in discussing ozone (p. 201) is very sensitive and characteristic for hydrogen peroxide and is carried out in the following manner: To 10 c.c. of a very dilute solution of H_2O_2 (even one drop in 400 c.c. of water) a drop of a 10 per cent. copper sulphate solution, and then, drop by drop, a saturated alcoholic solution of benzidine are added, until a slight turbidity is formed. The liquid is then shaken, when a deep blue precipitate is formed which is characteristic of H_2O_2 (Arnold and Mentzel, 1902).

The following is a fairly sensitive reaction: hydrogen peroxide is acidified in a test-tube, ether is added and then one or two drops of a dilute solution of potassium bichromate or chromic anhydride; on shaking, the new chromium compound thus formed (perchromic acid) dissolves in the ether, giving a blue colour, which, however, very quickly disappears.

Recently (1909) Charitschkoff found that even very small traces of hydrogen peroxide (0·03 per cent.) redden a piece of dry paper impregnated with a benzene solution of the cobalt salt of naphthenic acid (ozone does not react directly).

APPLICATIONS. Hydrogen peroxide is used for bleaching fine fabrics, especially woollen and silken fabrics, and ostrich feathers, ivory, etc. It is first made feebly alkaline with ammonia, and the textile fabrics to be dyed are then immersed for twelve hours in a cold bath containing 5 to 10 per cent. of the commercial hydrogen peroxide. If the solution is heated bleaching takes place in an hour, but then the bath which remains is very weak, whereas cold baths still contain much H_2O_2 after use, and can be used for successive operations by replenishing them with a little fresh H_2O_2. A more gradual reaction with less loss of oxygen is obtained by the use of hydrogen peroxide dissolved in 10 per cent. sodium acetate solution. Baths which have been used are preserved by acidifying them faintly with sulphuric acid. H_2O_2 also decomposes any residual SO_2 and Cl in fabrics which have been bleached by other means. It imparts to hair a beautiful yellowish golden colour, and is used for that purpose by women.

It is a good depolariser for galvanic batteries and a good antiseptic, especially in acid solution. It is also used for cleaning old blackened paintings, because it transforms the black lead sulphide (formed from white lead and hydrogen sulphide) into white lead sulphate.

Commercial hydrogen peroxide of a strength of 10 to 12 vols. costs from about £10 to £12 per ton.[1]

---

[1] The strength of hydrogen peroxide is determined by acidifying it strongly with sulphuric acid, diluting 5 c.c. with 50 c.c. of water, and then adding from a graduated burette $\frac{N}{10}$ potassium permanganate solution (3·17 grms. permanganate per litre), with stirring, until the last drop of permanganate is no longer decolorised. The calculation is then based on the following equation, which shows that 1 c.c. of $\frac{N}{10}$ solution of permanganate corresponds with 0·001701 grm. of H_2O_2 or with 0·5594 c.c. of oxygen:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

On multiplying the percentage weight of H_2O_2 by 3·29, one obtains the strength expressed in volumes of oxygen, that is, the number of litres of oxygen which 1 litre of the solution is capable of liberating. If the hydrogen peroxide has a strength of 3 per cent. by weight of H_2O_2, its strength expressed in volumes will be 9·87, that is, its strength, in round figures, is 10 vols.

In Italy 60 tons of hydrogen peroxide were manufactured in 1893, and in 1903 the production had already risen to 1370 tons, and in 1907 to 1800 tons, valued at £17,040; in 1908, however, the production decreased to 1470 tons, and in 1909 to 900 tons, rising in 1911 to 2266 tons. Belgium in 1909 produced 1500 tons of H_2O_2 (10–12 vols.), sold at £7 4*s*. per ton. The Chemische Werke in Vienna erected a 1000-h.p. plant for the production of H_2O_2 from persulphuric acid and enlarged it in 1911. In 1908 Germany exported 304 tons, and in 1909 about 446 tons.

PREPARATION. H_2O_2 is formed by adding barium peroxide to cold mineral acids, and sulphuric acid is used by preference because it forms insoluble barium sulphate, which is easily separated from the hydrogen peroxide dissolved in the water. By employing HCl, on the other hand, soluble barium chloride is formed which is difficult to separate.

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4.$$

It may also be produced by the action of carbon dioxide under pressure in presence of water:

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

A pure aqueous solution of hydrogen peroxide is obtained in practice by the action of sulphuric acid on the hydrate of barium peroxide in the following manner: The barium peroxide is finely powdered and added to a definite quantity of dilute HCl until this is almost completely neutralised; it is then filtered and the clear cold liquid is treated with baryta water until all the silica and the metallic oxides are precipitated. The liquid is again filtered and all the barium peroxide then precipitated as hydrate by adding excess of baryta water. It is collected on a filter, washed, and the moist hydrate then added little by little, with continuous agitation, to dilute sulphuric acid (1 : 5 H_2O), which is kept at a temperature below 10° by the addition of ice. Dilute hydrofluoric acid is now sometimes used instead of sulphuric acid, in which case the work is carried out in leaden vessels. When the acid (HF or H_2SO_4) is almost completely neutralised, the whole is stirred for some hours, allowed to settle and then filtered. If the exact elimination of all the acid which remains in solution is desired, this is achieved with a little barium peroxide and the liquid is again filtered. According to French patent No. 458,158 (1913) the following process is advantageous: To a solution of 30 litres of phosphoric acid (sp. gr. 1·7) in 60 litres of water are added, with stirring, 75 kilos of powdered BaO_2, the temperature being kept at 50–70°; by this means the iron, magnesium, calcium, aluminium, and silica present as impurities are precipitated or carried down with the barium phosphate, whereas in other processes they remain in solution (part of the phosphoric acid may be replaced by sulphuric acid). The resulting H_2O_2 has a concentration of 10–30 per cent.

Duprey obtains H_2O_2 by adding BaO_2 slowly to water saturated with CO_2 and Merck (German patent No. 179,771 of 1906) obtains a much better yield by pouring the CO_2 solution on to the BaO_2 (the reaction hence being always alkaline) or by using barium percarbonate.

Merck prepared pure 30 per cent. (100 vols.) hydrogen peroxide (called perhydrol) by adding the calculated quantity of sodium peroxide in small amounts to 20 per cent. sulphuric acid, which is kept cold; two-thirds of the sodium sulphate separates immediately in crystals. The liquid is filtered and distilled in a vacuum, the rest of the sodium sulphate—which is harmless and does not decompose the H_2O_2—being separated in the retort (best at − 10° with alcohol). The sodium salt may also be separated—by treatment with HF—as the slightly soluble $NaHF_2$, or by treatment with AlF_3, the NaF being then precipitated as cryolite (Hulin, German patent No. 132,090).

M. Traube (1889) observed that, when a hydrogen flame plays on the surface of water, hydrogen peroxide is formed, 0·75 per cent. of H_2O_2 being found in the flame. C. Engler (1900) obtained a better reaction by directing a hydrogen flame on to a block of ice. Nernst (1903) studied the equilibrium constants for the reaction, $2H_2O + O_2 \rightleftarrows 2H_2O_2$, and showed that at the absolute temperature 2784°, together with oxygen and water vapour at a pressure of 0·1 atmos., hydrogen peroxide can exist in a concentration of 0·6 per cent. Nernst (1905) and Franz Fischer (1906–1907) obtained 0·7 per cent. of H_2O_2 by passing a mixture of oxygen and water vapour at a velocity of 1 metre per second on to a surface heated by either the voltaic arc or an electric spark discharge or the oxy-hydrogen flame (Kahlbaum, Ger. patent No. 197,023, and F. Fischer, No. 228,425), but this method is not successful in practice. A. De Hemptinne (German patent No. 229,573, 1909) obtained 3 grams of H_2O_2 per kilowatt-hour by subjecting a mixture of hydrogen and oxygen (rendered inexplosible by means of excess of hydrogen) to the action of the dark discharge in apparatus resembling ozonisers (*see* p. 203); working at the temperature of liquid air. F. Fischer and M. Wolf (1911) obtained, from a mixture of 97 per cent. of H and 3 per cent. of O (by vol.), 86 per cent. H_2O_2 with a yield much better than that of Hemptinne.

Franz Fischer and O. Priess (1913) repeated M. Traube's experiments (1887) on the cathodic formation of H_2O_2 on electrolysis of dilute (1 per cent.) sulphuric acid with a current of air passing in contact with the cathode, and obtained better yields with respect to current by increasing the pressure (5 per cent. at 100 atmos.), 2·5 per cent. H_2O_2 being obtained.

At its present low price, sodium peroxide yields purer and perhaps cheaper hydrogen peroxide than BaO_2 does.

Very pure hydrogen peroxide of 10 per cent. strength is easily obtained by dissolving 170 grms. of sodium perborate and 60 grms. of citric acid in 1 litre of water.

For some years the manufacture of H_2O_2 by decomposition of persulphuric acid or persulphates (*q.v.*) has been of some importance. Berthelot observed that H_2O_2 is formed at the anode when a moderately concentrated solution of sulphuric acid is electrolysed. M. Traube and Richarz showed that, under these conditions, H_2O_2 is formed by an indirect reaction, viz., by the decomposition of the persulphuric acid first formed: $H_2S_2O_8$ (persulphuric acid) $+ H_2O = H_2SO_4 + H_2SO_5$ (Caro's acid); $H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$ (in the cold the reaction is reversible).

Nowadays hydrogen peroxide in 20 to 30 per cent. concentration is prepared industrially, and much more conveniently than by the old processes, by simple distillation of persulphuric acid, which is now manufactured electrolytically (*see later*) and which should be free from catalysts (German patent No. 199,598, 1906); hydrogen peroxide distils over and leaves sulphuric acid, which can be re-converted into persulphuric acid, so that only water and electrical energy are consumed.

A. Pietzsch and G. Adolph (German patents 241,702 and 256,148 and English patent 23,158, 1910–1911) obtained hydrogen peroxide of 30 per cent. strength by heating persulphates (obtainable pure and free from catalysts by crystallisation) with sulphuric acid.

L. Cambi and A. Spanò (1913) confirmed the influence of impurities (catalysts), especially ferric salts, on the yield of hydrogen peroxide obtained when persulphates are distilled with sulphuric acid, T. S. Price having observed that the decomposition of persulphuric acid and of Caro's acid by catalysts is more rapid in presence of hydrogen peroxide. Assuming a current yield of 40 per cent. for persulphuric acid and of 70 per cent. for potassium persulphate, they calculate that the energy consumed will be 28·1 to 33·8 kilowatt-hours per kilo of H_2O_2 distilled from persulphuric acid, and 16·1 to 22·5 kilowatt-hours per kilo of H_2O_2 from the persulphate.

According to English patent No. 22,019 (1909) the concentration of the H_2O_2 depends on that of the persulphate solution, but if a little hydrochloric acid is added to the latter the concentration of the hydrogen peroxide is increased without disturbing the electrolytic process.

Storage and Concentration. Hydrogen peroxide is always kept slightly acid, as it then retains its strength longer; even better than sulphuric acid for this purpose is a trace of tannin (German patent No. 196,370 of 1907), while Merck (1909) finds a small quantity of barbituric acid to be very effective. According to U.S. patent No. 1,002,854 (1911) the strength is well maintained if, for every kilo of 3 per cent. H_2O_2, 1 gram of benzoic, salicylic or phthalic acid (or one of their derivatives) is added. It has also been found (1914) that H_2O_2 in aqueous solution is stable, even in the hot, in presence of small quantities of stannous or titanium sulphate. In America traces of acetanilide are often added to preserve H_2O_2 and to allow of its distillation and concentration without great loss.

The liquid ordinarily maintains its strength satisfactorily on being stored in glass vessels coated internally with paraffin wax. It usually contains about 3 per cent. of H_2O_2, and is sold at a strength of 10 to 12 vols., which means that 1 litre of the hydrogen peroxide develops from 10 to 12 litres of oxygen.

Concentrated H_2O_2 may be obtained from this solution by distilling it at 75°, after having first separated all traces of alkali, metallic salts, or suspended matter. Hydrogen peroxide of 50 per cent. strength is thus obtained, and on redistilling it *in vacuo* (at a pressure of 5 to 7 cms. of mercury) the water first passes over and is followed by pure concentrated hydrogen peroxide. This may also be obtained from the 50 per cent. H_2O_2 by extracting it with ether. From the ethereal solution the ether is separated by distillation and the hydrogen peroxide which remains is in turn distilled at reduced pressure. A clear heavy liquid is thus obtained of sp. gr. 1·49 which boils at 69° at a pressure of 26 mm. and smells like nitric acid. It is soluble in water, alcohol, and ether, and contains up to 99 per cent. of H_2O_2. The concentration of hydrogen peroxide by means of a strong current of air at temperatures of 50° to 60° has recently been described (Ger. Pat. 219,154), H_2O_2 of 100 per cent. strength being then distilled at a temperature of 60° to 80°, still in the current of air.

Staedel obtains very pure crystallised 100 per cent. H_2O_2 by cooling the ordinary 96 per cent. product by means of a freezing mixture of ether and liquid carbon dioxide, this producing a temperature of 80° to 100° below zero. On then taking a minimal quantity of this solidified H_2O_2 and placing it in 96 per cent. hydrogen peroxide cooled to $-8°$, a mass of transparent crystals of chemically pure H_2O_2 immediately separates. This product melts at $-2°$. In contact with platinum black or manganese dioxide it explodes with great violence. It instantly sets fire to powdered magnesium, carbon, wool, etc., but does not react with reduced iron.

In 1911 Messrs. G. Richter (Budapest) placed on the market solid hydrogen peroxide under the name hyperol (Merck called it perhydrite), which is a compound of the peroxide (1 mol.) with urea (1 mol.)—prepared by Tanatar—stabilised with 0·08 per cent. of citric acid. Hyperol contains 34 per cent. H_2O_2 (theory = 35·9 per cent.), which can be extracted with ether. At 60° it begins to decompose with liberation of oxygen and at 85° the decomposition is complete. In some cases H_2O_2 is rendered stable by addition of a small quantity of an aromatic sulphonic acid.

HYDROGEN SULPHIDE: H_2S

This body is found free in nature, especially in volcanic gases and in some sulphuretted waters. In Italy such waters are found at Abano, Tabiano, etc. It is formed during the putrefaction of organic matter containing sulphur (albuminoids). This explains its presence in rotten eggs, closets, and latrines. During the putrefaction of organic matter sulphates, for instance, calcium sulphate, are also reduced, generating sulphides and hydrogen sulphide.

PHYSICAL PROPERTIES. Hydrogen sulphide is a colourless gas with a strong smell of rotten eggs, of density 1·19. If breathed in large quantities it acts as a soporific and a powerful poison, and if the pure gas is breathed it rapidly produces death (*see* Note, p. 207). It liquefies at a pressure of 17 atmospheres, or a temperature of $-74°$, yielding a colourless liquid of sp. gr. 0·9 which solidifies at $-91°$. One volume of water dissolves 3 to 4 vols. of H_2S gas.

CHEMICAL PROPERTIES. It burns with a bluish flame, giving sulphur dioxide: $H_2S + 3O = H_2O + SO_2$.

With a limited quantity of air, and if the flame of H_2S is cooled by introducing a cold body into it, the hydrogen alone is burned and the sulphur is deposited. The utilisation of the sulphur contained in the by-products of the Leblanc soda industry is based on this reaction. The aqueous solution of H_2S becomes turbid in contact with air by the deposition of very fine insoluble sulphur, $H_2S + O = H_2O + S$, and in order to preserve aqueous solutions of H_2S without alteration it is necessary to fill the bottles completely or close them hermetically.

The halogens act similarly to air, as we have seen in the preparation of hydriodic acid: $H_2S + I_2 = 2HI + S$.

H_2S is a good reducing agent, easily abstracting oxygen from other substances and reducing them to less highly oxidised compounds. This occurs with chromic, manganic, and nitric acids. Thus, on pouring a little fuming nitric acid into a cylinder containing dry H_2S, this catches fire with a slight explosion. In presence of porous materials H_2S is slowly oxidised in the air with ultimate formation of sulphuric acid. On the other hand, it is capable of reducing sulphuric acid, and for this reason this acid is not suitable for drying H_2S.

Being a reducing agent, it reduces solutions of potassium permanganate which transforms it into sulphuric acid. It decomposes with sulphur dioxide at the ordinary temperature, the sulphur of the H_2S and of the SO_2 being separated:

$$SO_2 + 2H_2S = 2H_2O + S_3.$$

This reaction explains the powerful deodorising action of sulphur dioxide in places smelling of H_2S. All that is necessary in order to eliminate such odours is to burn a little sulphur. The removal of the taste and smell of sulphur from wines by means of burning sulphur is due to the same cause. In many industries H_2S is separated from other gases by passing the mixture over hydrated ferric oxide or through alkaline solutions of ferric salts.

H_2S is a very weak acid which only faintly reddens blue litmus paper and forms two categories of salts with bases, namely, sulphides and hydrosulphides.

$KOH + H_2S = H_2O + KSH$ (potassium hydrosulphide or monopotassium sulphide)
$PbO + H_2S = H_2O + PbS$ (lead sulphide).

Almost all the metals form sulphides with H_2S with liberation of hydrogen, *e. g.*, $Pb + H_2S = PbS + H_2$.

The sulphides, then, are salts of hydrogen sulphide. They have characteristic colours varying with the nature of the metal. Thus zinc sulphide is white; cadmium sulphide, yellow; antimony sulphide, orange-red; lead sulphide, blackish brown; stannous sulphide, brown; stannic and arsenic sulphides, yellow, etc. Since, also, many metallic sulphides are insoluble in water and in acids, one may obtain precipitates from salts of other acids by treating them with hydrogen sulphide, which is therefore a valuable reagent in analytical chemistry. Very small traces of hydrogen sulphide may be detected by paper impregnated with lead acetate, which is immediately blackened.

Hydrogen sulphide is a weakly exothermic compound:

$$H_2 + S = H_2S \text{ gas} + 11 \text{ Kj and } H_2S + \text{aq.} = H_2S \text{ diss.} + 19 \text{ Kj},$$

that is, 30 Kj. (7170 cals.) in all. The heat of formation being very small, one can understand how it is that this compound is formed with difficulty from the elements H and S, and why it decomposes easily on heating (into H and S), and also why it is a weak acid.

It is a dibasic acid because its two hydrogen atoms may be replaced by one atom of a divalent metal or by two atoms of a monovalent metal. The behaviour of the dilute aqueous solution of its salts is, however, apparently abnormal, as is that of all weak dibasic or polybasic acids, and potassium or sodium sulphides in aqueous solution show an alkaline reaction on account of the hydrolytic dissociation (*see* p. 102), which is explained in the following manner:

The ions of H_2S in aqueous solution should be $H_2^{\cdot}$ and S'', where S'' represents the divalent anion of H_2S. In reality, however, the total dissociation is preceded by another phase, namely, $H_2S = H^{\cdot} + HS'$, where the anion HS' is monovalent and has a feeble acid reaction, in common with those of weak dibasic acids in general, which in aqueous solution are dissociated mainly in accordance with this first phase. The acid reaction is always due to the cation $H^\cdot$, and since that united to SH' is little or not at all dissociated, it holds that, in general, of two dibasic acids the one which is completely dissociated will be the more energetic, because it will liberate double the number of $H^\cdot$ ions, whilst only a small portion of the monovalent anion is dissociated further into the divalent anion: $HS' = H^\cdot + S''$. Thus, in aqueous solutions of H_2S there are many HS' and $H^\cdot$ ions and few S'' ions.

In the case of more energetic acids, on the other hand, the second phase of the dissociation preponderates. These considerations on ionic dissociation also explain the general behaviour of the two categories of salts of dibasic acids.

In the case of hydrogen sulphide, we have, for example, monosodium sulphide, NaHS (or sodium hydrosulphide, also called the acid sulphide or secondary sulphide of sodium), and disodium sulphide, Na_2S, also called the primary sulphide or neutral sulphide or normal sulphide of sodium. In aqueous solution the acid sulphide should show an acid reaction. Actually it shows neutral reaction because the weak anion SH' is only very slightly dissociated into S'' and $H^\cdot$; there are, therefore, very few $H^\cdot$ ions showing acid action, and even this dissociation is diminished because SH' becomes saturated with reformation of non-dissociated H_2S by the minimal quantities of $H^\cdot$ cations of the water itself (which under such conditions is very slightly dissociated into $H^\cdot$ and OH'); thus free hydroxyl ions of the water, which produce an alkaline reaction, remain, saturating and paralysing the weak acid action of the few $H^\cdot$ ions remaining free, so that the aqueous solutions of these monometallic sulphides (NaHS) thus show neutral reaction. The dimetallic or primary sulphides, on the contrary, show a markedly alkaline reaction in aqueous solution, because the two ions of the disodium sulphide, S'' and $Na_2^{\cdot\cdot}$, do not remain dissociated in this manner, as the anion S'' is readily hydrolysed by water, being transformed as follows: $S'' + H_2O = HS' + HO'$, and the SH' is further transformed in part into H_2S; hence the alkaline reaction of the hydroxyl (OH'), which gradually increases, turns red litmus paper blue. As a matter of fact the so-called neutral salts of weak acids, even of monobasic acids such as sodium hypochlorite, etc., show an alkaline reaction on account of pronounced *hydrolytic dissociation* in aqueous solution (pp. 102–103).

APPLICATIONS. Hydrogen sulphide is used in analytical laboratories, and also industrially for the purification of hydrochloric and sulphuric acids, etc.

PREPARATION. Hydrogen sulphide is formed in small quantities by passing hydrogen through boiling sulphur, or by mixing hydrogen and sulphur vapour at 500° in presence of porous bodies, such as pumice or bricks.

It is formed also by heating certain metallic sulphides to redness in presence of hydrogen: $Ag_2S + H_2 = H_2S + Ag_2$.

In the laboratory it is ordinarily prepared by acting on the metallic sulphides with an acid. Sulphuric acid or hydrochloric acid is commonly used with iron sulphide at the ordinary temperature in similar apparatus to that used for the preparation of hydrogen (p. 139):

$$FeS + SO_4H_2 = SO_4Fe + H_2S; \quad FeS + 2HCl = FeCl_2 + H_2S.$$

In this case the gas contains hydrogen proceeding from the action of the acid on the metallic iron always present as an impurity in the sulphide.

Pure hydrogen sulphide is obtained by heating antimony trisulphide with concentrated hydrochloric acid:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The sulphide is placed in a flask closed with a stopper carrying a thistle funnel for the introduction of the acid and a delivery tube for the gas, as in the preparation of chlorine (p. 152). The H_2S which is formed is first washed in water and then collected by displacement in cylinders filled with water.

Pure H_2S is also obtained by decomposing barium sulphide with pure hydrochloric acid: $BaS + 2HCl = BaCl_2 + H_2S$.

HYDROGEN PERSULPHIDE : H_2S_5

Just as hydrogen peroxide is formed by the action of acids on metallic peroxides, so by acting on certain metallic persulphides or polysulphides with acids, hydrogen persulphide is formed, but only the pentasulphide, H_2S_5, whatever may be the reacting polysulphides (Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5); probably other hypothetical hydrogen persulphides decompose, giving H_2S and H_2S_5 :

$$4Na_2S_2 + 8HCl = 8NaCl + 4H_2S_2;\ 4H_2S_2 = 3H_2S + H_2S_5.$$

This persulphide is an easily volatile, limpid yellow oil of sp. gr. 1·71. It decomposes easily in presence of moisture, giving sulphur and H_2S.

Bloch and Höhn (1908) prepared the persulphides S_3H_2 and S_2H_2, the existence of which was confirmed by Bruni and Borgo (1909).

HYDROGEN SELENIDE : H_2Se

This is obtained from its elements at 400°, or better still from iron selenide, FeSe, with hydrochloric acid. It is a colourless gas with a repugnant odour. It is a weak acid and more poisonous than H_2S. Pure selenium is liberated from its solutions by contact with the air. It precipitates many heavy metals in the form of *selenides.*

Selenious chloride, Se_2Cl_2, is known, and also selenium tetrachloride, $SeCl_4$, which is a solid, sublimes unchanged, and is more stable than sulphur tetrachloride.

HYDROGEN TELLURIDE : H_2Te

This gas is obtained mixed with oxygen by the action of hydrochloric acid on zinc telluride; it is a very poisonous, evil-smelling, colourless gas, and easily dissociates. It precipitates the salts of heavy metals from solution in the form of tellurides.

$TeCl_2$ and $TeCl_4$ are also known; the latter boils unaltered at 380°. Analogous compounds with Br, I, F, are also known.

HALOGEN COMPOUNDS OF SULPHUR

SULPHUR MONOCHLORIDE : S_2Cl_2. This is the most stable of these halogen compounds, and is obtained by passing dry chlorine over molten sulphur. It is a reddish-yellow liquid which fumes in the air and irritates the eyes. It has a specific gravity of 1·68 and boils at 138°.

It readily dissolves sulphur (66 per cent.), and the heavy solution obtained is used for the vulcanisation of rubber.

It decomposes with water as follows :

$$2S_2Cl_2 + 2H_2O = SO_2 + 3S + 4HCl.$$

SULPHUR DICHLORIDE : SCl_2. This compound is obtained by saturating the monochloride with chlorine at 6° to 10° and then driving off the excess of chlorine with CO_2 :

$$S_2Cl_2 + Cl_2 = 2SCl_2.$$

It is a reddish-brown liquid of sp. gr. 1·62, which boils at 64°, when it is partially decomposed into Cl_2 and S_2Cl_2; it is decomposed by water.

SULPHUR TETRACHLORIDE : SCl_4. This chloride is stable only below 0°; it is obtained by saturating sulphur chloride with chlorine at — 20°.

SULPHUR BROMIDE : S_2Br_2, is also known. It is a red liquid which boils at 190° to 200°.

Iodides of sulphur are not well known, but in 1900 Moissan appears to have prepared from its elements sulphur hexafluoride, SF_6, which is an almost inactive gas.

OXY-COMPOUNDS OF S, Se, Te

Whilst only two oxidised compounds of selenium and tellurium are known, namely, the dioxide and trioxide (SeO_2, SeO_3; TeO_2, TeO_3), four oxygen derivations of sulphur are known.

S_2O_3	SO_2	SO_3	S_2O_7
Sulphur sesquioxide	Sulphur dioxide or sulphurous anhydride	Sulphur trioxide or sulphuric anhydride	Sulphur heptoxide or persulphuric anhydride.

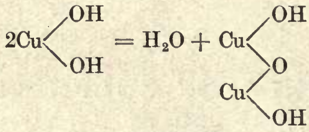
Excepting sulphur sesquioxide, all these oxides, which are also called anhydrides, generate the corresponding dibasic acids with one molecule of water. These acids give two series of salts: acid salts and normal salts.

There are, however, also other oxy-acids, which exist only in the form of salts, and of which the corresponding oxides or anhydrides are not yet known.

$S_2O_3H_2$, thiosulphuric acid (sometimes called hyposulphurous acid)
$S_2O_4H_2$, hydrosulphurous acid (the true hyposulphurous acid)
SO_3H_2, sulphurous acid
SO_4H_2, sulphuric acid
$S_2O_6H_2$, dithionic acid (hyposulphuric acid)
$S_3O_6H_2$, trithionic acid
$S_4O_6H_2$, tetrathionic acid
$S_5O_6H_2$, pentathionic acid
$S_2O_5H_2$, disulphurous acid (or pyrosulphurous acid, the salts of which are pyrosulphites or metabisulphites)
$S_2O_7H_2$, disulphuric acid
$S_2O_8H_2$, persulphuric acid
$S_2O_9H_2$, oxypersulphuric acid (Caro's acid)

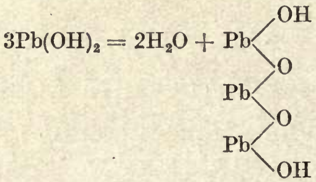
SALTS, ACIDS, AND BASES

We have seen how several molecules of a polybasic acid are able to condense and form polyacids, such as pyroantimonic, pyrophosphoric, and pyrosilicic acid, etc., and in the same way it is known that the polyacid bases, also called polyhydric bases, condense to form polybases or polyhydroxides:



$$2Cu{<}^{OH}_{OH} = H_2O + \begin{matrix}Cu{<}^{OH}_{O}\\ Cu{<}^{O}_{OH}\end{matrix}$$

;

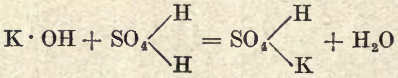


$$3Pb(OH)_2 = 2H_2O + \begin{matrix}Pb{<}^{OH}_{O}\\ Pb{<}^{O}_{O}\\ Pb{<}^{O}_{OH}\end{matrix}$$

From these polyhydroxides basic salts are obtained by the replacement of a portion of the hydroxyl groups by acid residues.

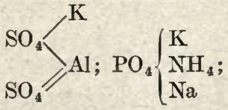
The metals easily form halogen combinations (chlorides, bromides, iodides, etc., which are non-oxygenated salts) either by the direct interaction of their elements or by the action of the halogen acids on either the metals or the corresponding oxides and carbonates; some of these combinations are easily obtained by the action of the halogen on a mixture of metallic oxide and carbon.

In the formation of salts from acids and bases there is generally separation of one or more molecules of water formed from one or more hydrogen atoms from the acid and one or more hydroxyl groups from the base:

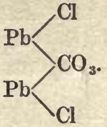
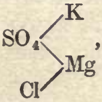


$$K\cdot OH + SO_4{<}^{H}_{H} = SO_4{<}^{H}_{K} + H_2O \quad ; \quad K\cdot OH + HCl = KCl + H_2O.$$

Mixed salts or *Double salts* are obtained when the hydrogen atoms of a polybasic acid are replaced by atoms of more than one metal, for example,



$$\begin{matrix}SO_4{<}^{K}\\ SO_4{\diagup}\end{matrix}{>}Al; \quad PO_4\begin{cases}K\\ NH_4;\\ Na\end{cases}$$

also when the hydroxyl groups of a polybase are replaced by acid residues of varying character, for example,  $\begin{array}{l}\mathrm{Pb}<^{\mathrm{Cl}}\\ \qquad >\mathrm{CO_3}\\ \mathrm{Pb}<_{\mathrm{Cl}}\end{array}$. However, such constitutions for the double salts are applicable only to the solid crystallised state, because in aqueous solution they form, not the corresponding characteristic ions, but ions which are the same as those of the simple salts, that is, of potassium sulphate, aluminium sulphate, potassium phosphate, ammonium phosphate, etc. In dilute solution the size of the molecule is actually found by cryoscopic determination to correspond, not with that of the double salt, but with those of the simple salts. The double salts, however, separate from concentrated solutions of the simple salts when one of these salts is in excess. In general double salts have two similar metallic or acid residues. Very occasionally double salts are met with which contain simultaneously both acid and basic residues all different, such as,  $\mathrm{SO_4}<^{\mathrm{K}}_{\mathrm{Mg}-\mathrm{Cl}}$, and the formulæ of these special double salts are written as molecules of the component salts, separated by a comma: $\mathrm{SO_4Mg,KCl}$. Certain complex double salts are also known which dissociate in solution into special ions different from those of the corresponding simple salts.

The property possessed by certain substances of forming double or complex salts which are more soluble than those of the individual simple salts is utilised in practice, as in some cases the solubility of a given salt can thus be considerably increased.

NOMENCLATURE OF SALTS, ACIDS, AND BASES. In the denomination or nomenclature of salts, the name of the acid is formed from the name of the corresponding elements modified by a suffix. The names of the more stable and better known acids terminate in *ic*, for example, hydrochloric, chloric, sulphuric, and nitric acids, etc.; the salts corresponding with the non-oxygenated acids change the suffix *ic* into *ide* (chloride, sulphide, iodide, etc.), whilst in those derived from the oxy-acids, the suffix is changed to *ate* (chlorate, sulphate, arsenate, carbonate, etc.). The acids which contain less oxygen have the suffix *ous* (nitrous, sulphurous, arsenious, etc.), and the names of the salts corresponding with them end in *ite* (nitrite, sulphite, arsenite, etc.). On the other hand, the acids containing more oxygen take the prefix *per* (persulphuric, perchloric acids, etc.), and the corresponding salts change their suffix into *ate* whilst retaining the prefix *per* (persulphate, perchlorate). Acids containing a minimum of oxygen take the suffix *ous*, together with the prefix *hypo* (hyposulphurous, hypochlorous, hyponitrous acids, etc.), and in their salts the suffix is replaced by *ite* (hyposulphite, hypochlorite, hyponitrite, etc.). Many metallic oxides which contain a maximum amount of oxygen and are able to give up a part of it readily, so that they act as energetic oxidisers, are called peroxides.

SULPHUR DIOXIDE: SO_2

Sulphur dioxide is found free in considerable quantities in nature, in certain volcanic emanations, and being an exothermic compound it is readily formed together with a trace (sometimes 2–8 per cent.) of SO_3 by burning sulphur in the air: $S + O_2 = SO_2 + 71{\cdot}7$ Cals. for monoclinic and 71·08 Cals. for rhombic sulphur, and 1 kilo of sulphur develops 2165 Cals. on burning. The formation of SO_2 by burning solid sulphur occurs without change of volume, that is, from 1 vol. of O_2 1 vol. of SO_2 is obtained, and from this its composition may also be deduced, because if SO_3 were formed then from 3 vols. of O_2 one would obtain 2 vols. of SO_3. SO_2 is manufactured industrially by roasting certain metallic sulphides, especially pyrites (sulphides of iron, copper, etc.), in special furnaces: $CuS + 3O = CuO + SO_2$, and also:

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2 + 419{\cdot}8 \text{ cals.},$$

that is, 105 cals. for each molecule of SO_2 (*see* Note, p. 177).

Pyrites burnt in lumps in pyrites burners sometimes give as much as 13 per cent. of SO_3, whilst much less of the latter (below 3 per cent.) is formed if the powdered pyrites is burnt; if SO_3 or H_2SO_4 vapour is present, the gas forms clouds.

The SO_2 from large copper smelting plants is sometimes utilised for the manufacture of sulphuric acid in lead chambers, but cannot be used for the manufacture of catalytic sulphuric acid, because the catalyst soon becomes covered by powdered zinc oxide and the excessive amount of moisture renders the acid very dilute.

A regular development of SO_2 is conveniently obtained in the laboratory by heating one part of mercury or of copper turnings with three parts of strong sulphuric acid in a flask:

$$Cu + 2SO_4H_2 = CuSO_4 + 2H_2O + SO_2,$$

a small amount of cuprous sulphide, Cu_2S, being also formed.

Pure sulphur dioxide is obtained also by decomposing sulphites and bisulphites with mineral acids, or by reducing sulphuric acid by heating it with charcoal in a flask: $2SO_4H_2 + C = 2SO_2 + CO_2 + 2H_2O$.

Since CO_2 is formed together with SO_2 in this manner and is difficult to separate, this method is employed only when a dilute aqueous solution of SO_2 is to be prepared, in which case the gaseous mixture is passed through water, in which the CO_2 is only slightly soluble.

SO_2 has also been prepared industrially by decomposing sulphuric acid by heat (Debray and Deville, p. 195), being then used to manufacture sulphur trioxide (*see below*).

PHYSICAL PROPERTIES. Dry sulphur dioxide is a colourless gas of suffocating, disagreeable, and penetrating smell; it gives white fumes in moist air; its density at 15° is 2·228 [theoretically—from the mol. wt.—2·2133 (*see* p. 34), the difference being due to its proximity to the condensation point] and its specific heat with respect to air, 0·3414; it is harmful for respiration and to vegetation, and is employed as an antiseptic in various industries (beer, wine, meat, etc.).

It is readily liquefied by cooling it with ice and salt, or at a pressure of only 2·72 atmospheres at + 15°.

In the liquid state it is colourless and fairly mobile, has the specific gravity 1·435 at 0° and 1·396 at 15°, boils at − 10°, and solidifies at − 76°. It absorbs much heat (91·7 Cals.) on evaporation, and on this account is employed in ice factories for the production of cold (*see* Ice).

On pouring liquid SO_2 on to mercury and accelerating the evaporation by means of a jet of air, the mercury is solidified (− 40°).

One volume of water at 0° dissolves 69 vols. of SO_2, at 5° 60 vols., at 10° 51·4, at 15° 43·5, and at 20° 36 vols. In order to obtain more concentrated solutions it is necessary to cool the water, because the gas is less soluble in hot water, and at a certain temperature all the SO_2 is liberated. At a temperature of 20° the saturated solution contains 8·6 per cent. by weight of SO_2, at 40° only 6·1 per cent., and at 100° only 0·1 per cent.; at 15° the saturated solution of specific gravity 1·056 contains 11 per cent. of

SO_2.[1] Alcohol at 0° dissolves 54 per cent. of SO_2 and at 26° only 26·5 per cent. On dissolution in water sulphur dioxide forms sulphurous acid: $H_2O + SO_2 = SO_3H_2$, but this acid has not yet been isolated as such. Aqueous solutions preserve their strength almost unchanged for several months if 5 per cent. of glycerine is added.

On dissolving in water SO_2 develops 32 Kj (7700 cals.). Concentrated sulphuric acid dissolves only 0·009 per cent. of SO_2. The liquefied anhydride dissolves only 1·04 per cent. of water, but any quantity whatsoever of SO_3.

CHEMICAL PROPERTIES. When heated with oxygen or air in presence of platinum sponge, or platinised asbestos, iron oxide, or certain other catalytic substances, SO_2 is completely oxidised, giving sulphur trioxide: $SO_2 + O = SO_3$. The aqueous solution is also slowly oxidised in the air, giving sulphuric acid: $SO_2 + O + H_2O = H_2SO_4$, and more easily by the action of the halogens: $SO_2 + 2H_2O + I_2 = SO_4H_2 + 2HI$, so that the iodine solution is decolorised.

Sulphur dioxide is a good reducing agent, because it removes oxygen from many substances, being itself oxidised, and thus decolorises solutions of potassium permanganate yielding manganous salts:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

The natural colouring matters are also decolorised by SO_2, for instance, those of many flowers, of wine, of wool, and of raw silk, which are bleached in this manner. Leuco-compounds are formed in this way which are not very stable, but which are soluble in dilute sulphuric acid and liable to re-oxidisation by the air. Bleaching by this means is hence not very durable unless these products are removed by washing with water or dilute sulphuric acid.

SO_2 may be reduced in turn by more energetic reducing agents, such as H_2S, with separation of sulphur: $SO_2 + 2H_2S = 2H_2O + 3S$. The gas does not maintain combustion and may therefore be used to extinguish fires.

Traces of SO_2 are detected by treating even very dilute solutions with a few crystals of potassium iodate and then a few drops of HCl, and shaking with a little chloroform; this dissolves the liberated iodine and acquires a violet colour.

APPLICATIONS OF SO_2. The bulk of the SO_2 produced is used directly on the spot for the manufacture of sulphuric acid. It is also used in paper works for the bleaching of straw and of wood; in alum factories; for the preservation of fruit, beer, wine,

---

[1] In the case of pure aqueous solutions the amount of SO_2 present may be determined with the help of the following table, which applies to a temperature of 15·5°:

density 1·0056 = 1 % SO_2
,, 1·0113 = 2 % ,,
,, 1·0168 = 3 % ,,
,, 1·0221 = 4 % ,,

density 1·0275 = 5 % SO_2
,, 1·0328 = 6 % ,,
,, 1·0377 = 7 % ,,
,, 1·0426 = 8 % ,,

density 1·0474 = 9 % SO_2
,, 1·0520 = 10 % ,,
,, 1·0560 = 11 % ,,
,, 1·0668 = 13 % at 11°

The strength of the aqueous solution is determined with greater exactitude, even when other substances are present, by means of standard iodine solution, into which the solution of SO_2 is dropped with continuous stirring, $SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$, and also by determining the total acidity with $\frac{N}{10}$ sodium hydroxide in presence of phenolphthalein as indicator. In this way any sulphuric acid which may have been present in the solution of SO_2 is also determined, whilst the amount of the latter is found from the amount of iodine used, by means of the above equation.

The strength of liquid anhydrous sulphurous acid is determined by first weighing a given quantity in a tared pipette with two stop-cocks, and then allowing the SO_2 as it evaporates to bubble through an $\frac{N}{10}$ solution of iodine, previously passing it through two weighed calcium chloride tubes in order to absorb the moisture, which is weighed separately; the excess of iodine is titrated back with $\frac{N}{10}$ sodium thiosulphate, and the result calculated: 1 c.c. of $\frac{N}{10}$ iodine solution corresponds with 1·0946 c.c. of dry SO_2 at 0° and 760 mm. Anything which remains in the pipette after this has been heated to 70° to 80° is sulphuric acid and tar, which, after weighing, is removed with hot water and the sulphuric acid titrated. The tar may also be finally extracted with ether and weighed after evaporating the latter.

meat, dextrin, and sugar syrups (being a good antiseptic), and also for the extraction of calcium phosphate from bones in the manufacture of glue. It is also used for bleaching wool, silk, and straw hats. It is used in sugar refineries because it has very little inverting action on the sugar; it is also employed in tartaric acid factories, etc. Its use has recently been proposed for the interruption of the fermentation of grape juice (*must*) in wine manufacture.

The main consumption of liquid SO_2 takes place in Pictet's ice machines and in the manufacture of cellulose. It has the property of dissolving oils and fats under pressure, but is unable to compete in this respect with benzine and carbon disulphide. Liquid SO_2 is now used for the rapid disinfection of ships and for destroying the rats which infest them. It will probably acquire great importance in the future through its use in connection with steam-engines patented by Behrend and Zimmerman, serving to increase the efficiency of the steam-engines by utilising the heat which would otherwise be lost, for the evaporation of liquid SO_2 and the production of strong pressure in a motor supplementary to the engine itself. When it has been thus utilised the SO_2 is again liquefied in a condenser with cold water and re-utilised.

STATISTICS AND PRICES. Liquid sulphur dioxide comes on to the market to-day in steel cylinders at about £1 5*s.* to £1 9*s.* per 100 kilos. The empty steel bombs, tested to thirty atmospheres, cost £4 for a capacity of 100 kilos, or £1 10*s.* for a capacity of 10 kilos. These bombs are let out on hire by the manufacturers, who after three months demand a rent of 1*s.* to 2*s.* per month.

According to law (in Italy) the bomb may not contain more than 1·25 kilos of SO_2 per litre total capacity, so that a space of SO_2 vapour may be left, and explosions due to large variations of temperature thus avoided; at 15° the coefficient of expansion is 0·00186 and at 95° is similar to that of gases.

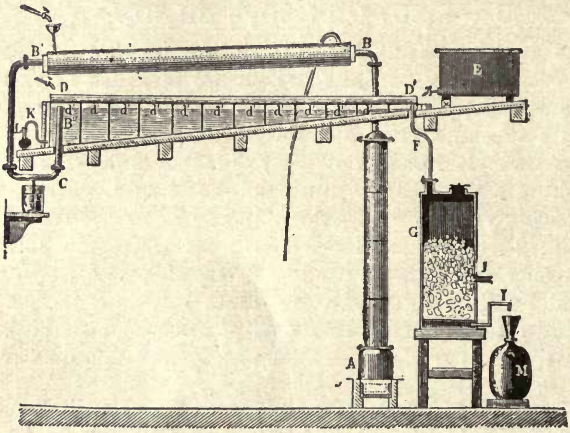


Fig. 95.

In the mines of Oppeln (Prussia) in 1893 1600 tons of liquid SO_2 were produced. Very large quantities are prepared in the factory of W. Grillo of Hamborn; in 1910 2357 tons of liquid SO_2 were prepared in Germany alone from pyrites burners. In Italy 13 tons of liquid SO_2 were produced in 1902, and in 1910 1000 tons, 100 tons being made by the Nobel Company of Avigliana (where the production was abandoned later). In 1904 50·7 tons were imported, of the value of £1217, in 1906 34·4 tons at 28*s.* per 100 kilos, in 1908 about 51·3 tons of the value of £1088, in 1910 75·7 tons, in 1911 108·9 tons, in 1912 74·1 tons, in 1913 122 tons, and in 1914 145 tons (£2608). The cost of production is about 4*s.* per 100 kilos, and the sale price for large quantities was £5 12*s.* per ton in 1899 in tank-wagons at the works. In Italy it is sold in steel cylinders containing 25 or 50 kilos at 5·8*d.* per kilo; in order that a factory making liquid sulphur dioxide may be profitable it must produce at least about 1 ton per day.

INDUSTRIAL PREPARATION OF SO_2. The preparation of SO_2 for the manufacture of sulphuric acid, which constitutes the main consumption of sulphur dioxide, will be described later in speaking of that acid. We shall confine ourselves now to the preparation of concentrated aqueous solutions of SO_2 and of pure liquefied SO_2, which is employed in many industries.

A concentrated aqueous solution of sulphur dioxide is obtained by the direct combustion of sulphur, making use, for example, of the apparatus of Hatschek, which has been applied in many industries.

The sulphur is burned on iron plates or pans arranged in a chamber, *A* (Fig. 95), surmounted by a leaden chimney some metres in height in order to obtain a sufficient draught.

The SO_2 passes along the condenser, *BB′*, where the small quantities of sulphuric acid formed are condensed. These collect in a suitable vessel with a hydraulic seal in the lower part of the tube *C*. The SO_2, on the other hand, passes into the upper part of the condenser, *d′*, formed of a wooden box lined with lead and covered by a shallow pan, *D*, along which water runs continuously, cooling the gas. The condenser is divided into several compartments with vertical walls which join opposite sides of the condenser alternately in such a manner that the water which enters continuously at *E* and escapes saturated with SO_2 from the tube *K* is forced to traverse a zigzag path in the opposite direction to the gas passing continuously over its surface. The chambers gradually diminish in volume because the gaseous SO_2 diminishes in quantity as it is absorbed. The aqueous solution of SO_2 escapes from the tube *L*, while the non-absorbed SO_2 passes through the tube *F* into the large vessel *G* containing soda crystals, which with SO_2 form sodium sulphite or bisulphite (*see* Part III).

Theoretically 4 cu. metres of air are required per kilo of sulphur, but in practice about 5½ cu. metres are employed. In order that the work may be carried on continuously in the hot furnace, molten sulphur may gradually be added.

This method is economical, but it does not yield very concentrated solutions, and the decomposition of sulphuric acid by carbon is in many cases preferred. H_2SO_4 of 62° Bé. (sp. gr. 1·75) is employed: $2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$; if the acid is more concentrated CO is also formed: $H_2SO_4 + C = SO_2 + H_2O + CO$, whilst if it is very dilute H_2S is formed: $H_2SO_4 + 2C = H_2S + 2CO_2$. The operation is carried out in a very simple apparatus; a species of stoneware receiver (*see* p. 176) with two necks containing wood-charcoal is immersed in a sand-bath placed over a furnace. Sulphuric acid is allowed to drop slowly on to the carbon and this is heated. The gaseous SO_2 is condensed in three successive communicating receivers containing water. In the first the sulphuric acid carried over by the gas is retained; in the second and third the concentrated solution of SO_2 is formed and is removed by means of cocks fitted into the base of the receivers.

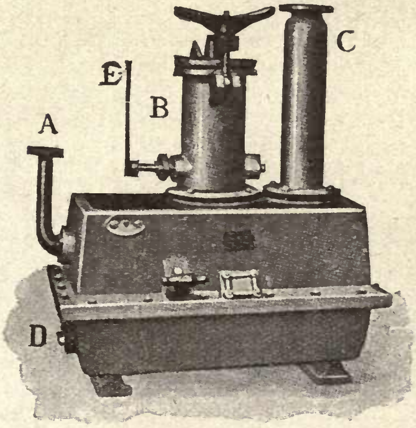


FIG. 96.

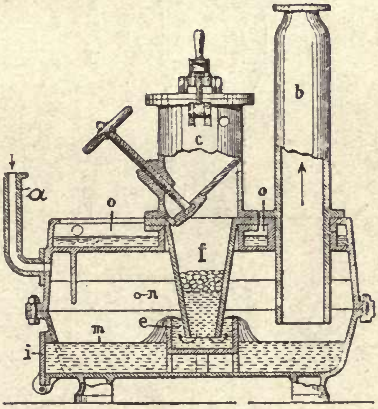


FIG. 97.

A very convenient apparatus which is largely used and is suitable for either small or large quantities of sulphur (from 10 to 500 kilos) is that illustrated in Fig. 96. The two superposed halves of the furnace are made of cast-iron and are united by bolts. In the interior is a pan which receives the sulphur from the cylinder *B*, furnished with a revolving plate which can be turned by the handle *E* in such a way as to charge the cylinder *B*, even during working. When the mouth of *B* is closed the sulphur may be discharged into the interior of the furnace by turning the handle *E*. By opening the aperture *D* momentarily the combustion may be started by means of a red-hot iron rod, this hole being then closed and a regular current of air passed through *A* from a compressor or pump in order to burn the sulphur. The sulphur dioxide escapes through the tube *C*, and is conducted to the absorption or condensing apparatus.

In order to avoid too great a rise of temperature in the interior of the furnace, which would damage the pan and cause the sulphur to distil, the whole apparatus is completely immersed in a box through which cold water runs. A furnace which burns 100 kilos of sulphur in twenty-four hours costs about £24. Various improvements on this furnace will be found described in Ger. Pat. 196,371 of 1907–1908, and the section is illustrated in Fig. 97. The sulphur is lighted through the aperture *n*, and during combustion the furnace is fed with lump sulphur through *c* into a funnel, *f*, which always dips in the molten sulphur accumulated in the pan *e*. As the sulphur melts, it overflows into the furnace at *m*. Cooling is effected by passing water over the cover *o*, and air is passed in under pressure in order to burn any sublimed sulphur in the delivery tube *b*.

PREPARATION OF LIQUID SULPHUR DIOXIDE. In 1878 R. Pictet prepared liquid sulphur dioxide for his ice machines by allowing a continuous stream of strong sulphuric acid to pass on to molten sulphur heated in a cast-iron retort to 400°: $2H_2SO_4 + S = 3SO_2 + 2H_2O$.

The strong sulphuric acid serves also to dry the SO_2, and to retain the sublimed sulphur carried over by the gas; this is passed through a loose filter of cotton wool. The gas is then cooled to − 10° and compressed in order to obtain the liquid. R. Pictet also proposed to separate pure SO_2 from dilute aqueous solutions by separation of the water by freezing. Certain French works use the Melsens-Pictet process.

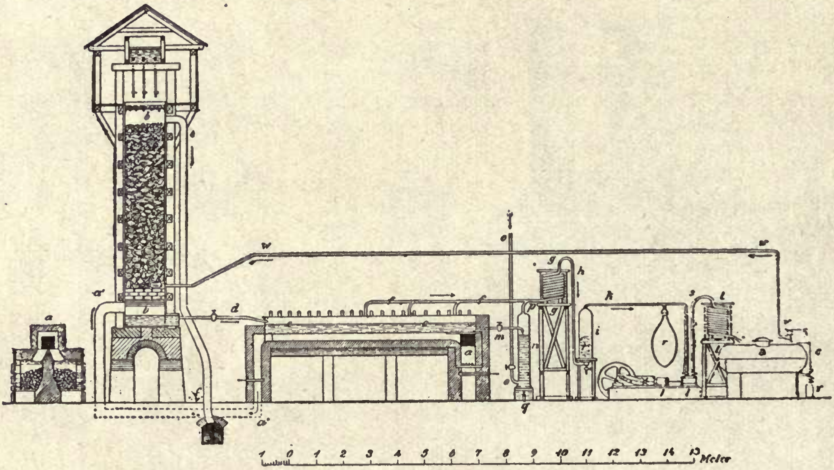


FIG. 98.

The gases obtained in the combustion of pyrites contain less than 9 per cent. by volume of SO_2 and with water give very dilute solutions containing about 2 per cent. by weight of SO_2, whilst by the above process the solutions contain from 10 to 12 per cent. by weight. The process of Hänisch and Schroeder patented in 1883 and perfected later (Ger. Pat. 52,025 of 1889) is of more industrial importance.

Hänisch and Schroeder prepare liquid sulphur dioxide even from gases containing only 4 per cent. by volume of SO_2. The complete plant is shown in Fig. 98. The very hot gases from the pyrites burner *a* (to the left of the figure) are passed through suitable flues (not indicated in the figure) under a leaden basin, *e*, which contains an aqueous solution of SO_2 to be evaporated. The somewhat cool gases then pass through the tube *a′* into the lower part of the lead tower *b*, which is filled with coke and in which they rise and meet a fine spray of water falling from the top and dissolving all the SO_2. The other gases, *O* and *N*, pass to the chimney through the pipe *c*. The dilute aqueous SO_2 solution collects in the pan *b*, at the base of the tower, and passes thence through the tube *d* into the evaporating pan *e*. The mixture of water vapour and SO_2 which is formed enters the bottom of the condensing coil *g* through the tube *f*. The condensing tower is nowadays built differently from the one indicated in the figure, and, together with the other small tower, *n*, is replaced by a much more effective tower described below. In any case moist SO_2 vapour alone escapes from the top of the tower through the tube *h*, and is dried in the cylindrical vessel *i*, through which a spray of strong sulphuric acid continuously falls. The dry SO_2 is absorbed and compressed by the pump *l*, and then enters the coil *t*, surrounded by cold water; here it is liquefied and accumulates in the iron receiver *u*. The iron cylinders *v*, in which the liquid SO_2 is sold, are filled by means of suitable cocks, as is seen in the figure, and the air which escapes from the cylinders enters the vessel *u*, and together with a small amount of SO_2 vapour passes into the pipe *w*, provided with pressure-valves, and from there is carried to the base of the tower *b*.

In order that the pressure in the whole plant may be maintained fairly constant and not be unduly affected by the action of the pump, a large rubber bag, *r*, is interposed between the pump and the rest of the plant, this serving to lessen the oscillations of pressure.

Hänisch and Schroeder separate the SO_2 in the tower *g* by means of a very ingenious principle. This tower now takes the form indicated in Fig. 99. A very hot mixture of steam and SO_2 enters the bottom of the leaden tower, the lower half of which is filled with clay or stone plates in order to lengthen the passage of the gas, while the upper part contains coke. A very fine spray of cold water falls from the top of the tower in such quantity that it just serves to condense the water vapour, which then gives up its heat of evaporation (536 cals.) to the condensed water and maintains it at a temperature of about 100°. At this temperature, however, the water cannot retain more than 0·1 to 0·5 per cent. of SO_2, and almost pure water collects at the bottom of the tower, whilst only pure SO_2 mixed with a very small quantity of water vapour escapes from the top and is completely dried with H_2SO_4 in the cylinder *i*, shown in the preceding figure. Thus, in the older plant the condensed water enters the cylinder *n*, into which a jet of steam is passed from *o* and carries over the last traces of SO_2. When the new condensing tower is used this operation is unnecessary.

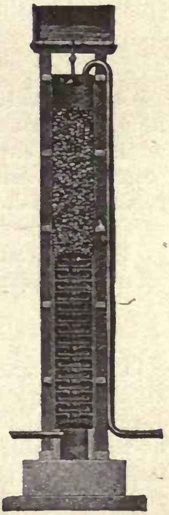


FIG. 99.

A proposal has been made (Ger. Pat. 160,940) to absorb the SO_2 from very dilute but dry gaseous mixtures by means of dicalcium phosphate :

$$2CaHPO_4 + 2SO_2 + 2H_2O = \underset{\substack{\text{monocalcium}\\ \text{phosphate}}}{Ca(PO_4H_2)_2} + \underset{\substack{\text{calcium}\\ \text{sulphite}}}{Ca(SO_3H)_2}.$$

On heating this product to 100° all the SO_2 is driven off from the sulphite, and the dicalcium phosphate is regenerated.

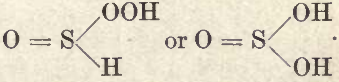
SULPHUROUS ACID : H_2SO_3

The acid is not known in the free state, but is supposed to exist in aqueous solutions obtained by saturating water with SO_2. With time, and in the light, the solution decomposes with separation of sulphur and formation of sulphuric acid : $3SO_2 + 2H_2O = 2SO_4H_2 + S$.

On the other hand, the salts derived from this acid are well known (Part III), *e. g.*, acid sodium sulphite, $NaHSO_3$ (also called bisulphite), and the normal sulphite, Na_2SO_3, both of which evolve SO_2 copiously when treated with mineral acids :

$$SO_3Na_2 + 2HCl = 2NaCl + H_2O + SO_2.$$

The constitutional formula of sulphurous acid is supposed to correspond with one or other of the two following isomerides :



$$O = S\begin{smallmatrix}OOH\\ H\end{smallmatrix} \quad \text{or} \quad O = S\begin{smallmatrix}OH\\ OH\end{smallmatrix}.$$

Certain organic derivatives correspond with the second formula, and certain inorganic salts with the first (asymmetric) formula.

Sulphurous acid is a weak acid which is not able to neutralise energetic bases completely, so that the normal sulphites show a weak alkaline reaction, whilst the bisulphites or acid sulphites show a faint acid reaction; this is easily explained according to the ionic theory by the hydrolysis which occurs in aqueous solution, as has been explained at length for the sulphides (*see* pp. 271–272). Thus sodium sulphite, which might be expected to show a neutral reaction, actually shows an alkaline reaction in aqueous solution, because it is hydrolysed and alkaline hydroxyl ions are formed:

$$Na_2^{\cdot\cdot}SO_3'' + H_2O = Na^{\cdot}HSO_3' + Na^{\cdot}OH'.$$

HYDROSULPHUROUS ACID: $H_2S_2O_4$

As early as 1852 Schönbein observed that iron and zinc dissolve in an aqueous solution of sulphurous acid without development of hydrogen, and that the yellow liquid which results has a strong reducing and bleaching action (especially for indigo), this being much greater than that of SO_2; further, it is easily decomposed with separation of sulphur and sulphurous acid. The solution in question contains hydrosulphurous acid, the composition of which is known from that of its salts.

The salts, called *hydrosulphites*, are stable, and are largely used in various industries, sometimes under the name of hyposulphites (*see* Part III).

SULPHUR SESQUIOXIDE: S_2O_3

This substance is obtained as a blue mass, at first liquid and then solid, on dissolving sulphur in liquid sulphur trioxide. It is readily decomposed into SO_2 and sulphur. It decomposes violently with water, forming SO_2, S, H_2SO_4, and polythionic acids. It dissolves in fuming sulphuric acid to form a blue liquid. It is used in the manufacture of aniline colours (naphthazarine).

SULPHURIC ACID: H_2SO_4

At the end of the eighth century Gebir knew and prepared sulphuric acid, which he obtained by distilling alum and iron sulphate.

About the year 1450 Basil Valentine obtained it by burning sulphur in presence of nitre. Angelo Sala[1] obtained it in 1613 by burning sulphur in presence of steam and an excess of air, and in 1620 Lefèvre and Lémery perfected Sala's method by employing nitre, as is still done to-day. It is found free in nature in certain rivers in America (Rio Canea and Rio Vinagre) which carry down to the sea daily 37,000 kilos of sulphuric acid and 31,000 kilos of hydrochloric acid. The mineral waters of Levico in Trent, which are used for baths, contain as much as 8·33 grms. of free sulphuric acid per litre.

It is also found in certain Sicilian snails called *Aplisia*: the juice which issues from the aperture of their shells produces a strong effervescence with marble, as it contains as much as 4 per cent. of free sulphuric acid.

It is much diffused as calcium sulphate in minerals (gypsum, SO_4Ca, $2H_2O$, and anhydrite, SO_4Ca).

PHYSICAL PROPERTIES. The sulphuric acid which is obtained in lead chambers (*see below*) contains about 63 per cent., and in order to concentrate it, it must be distilled. It is impossible, however, to obtain by distillation an acid containing more than 98·5 per cent. of H_2SO_4, because even on distilling 100 per cent. acid (obtained by other means) an acid of 98·6 per cent. is always obtained, the rest being water formed by the decomposition of the acid, which has a specific gravity of 1·842 at 12°. In order to separate this final portion of water, the acid is cooled to − 10° and a few crystals of purest frozen sulphuric acid are then added. This causes the crystallisation of sulphuric acid free from water from the remaining liquid, from which it is separated by means of a centrifuge (Lunge). The acid so obtained is the so-called sulphuric acid monohydrate ($SO_3 + H_2O$). This contains 100 per cent. of H_2SO_4, has a specific gravity of 1·838 at 15°, and is thus less dense than the distilled acid, although it is more concentrated.

---

[1] Sala was a medical man and chemist of Vincentio, who lived at the Court of Mecklenburg and introduced the use of silver nitrate into medicine.

The monohydrate yields vapours of SO_3 and water already at 40°. It commences to boil at 290°, and at 338° gives in this way an acid containing 1·5 to 2 per cent. of water. At 416° it dissociates completely into SO_3 and H_2O. The acid of 50° Bé. commences to boil at 147° and acid of 60° Bé. at 200°, while acid of 66° Bé (98·5 per cent.) has both specific gravity and boiling-point (338°) higher than those of the monohydrate.

The concentrated acid is a dense oily liquid; when it contains 15 per cent. of water a crystalline hydrate, $SO_4H_2 + H_2O$, separates at 0°. This melts at + 8°; the hydrate, $SO_4H_2 + 2H_2O$, is also known. Acid of 60° Bé. easily freezes in winter and bursts the carboys in which it is contained; if it is somewhat more or somewhat less concentrated it does not freeze.

When it is mixed with water much heat is evolved with contraction of the total volume (8 per cent. of contraction with 27 per cent. H_2O), and in order to prepare the mixture the acid should always be poured slowly into the water, with thorough stirring, and not the water into the acid, in order to avoid spurting of the acid in consequence of the large quantity of heat suddenly developed.

When 1 mol. (98 grms.) of sulphuric acid monohydrate is mixed with 1 mol. of water (18 grms.) 26·2 Kj. (6262 cals.) are developed, with 10 mols. of water 63 Kj., with 100 mols. (that is, 1800 grms. of water) 70·5 Kj., and with 1000 mols. 74·5 Kj. (that is, 17,800 cals.), in consequence of the formation of a progressive series of hydrates and of the contraction of volume (*see* p. 27).

On the other hand, when concentrated sulphuric acid is mixed with snow, a very high degree of cold is produced, the heat of solution of the acid being lower than the heat of fusion of the snow.

The specific heat of the monohydrate is 0·3315 and that of the dilute acid (1 to 2 of water) 0·725, whilst that of the 1 acid to 20 water mixture is 0·955, the value for water being 1.

The heat of formation of H_2SO_4 is 596 Kj. (= 142,500 cals.).

The vapour pressure of the water in 60 per cent. acid is 3 mm. of mercury at 20°, 25 mm. at 60°, and 143 mm. at 100°. In acid containing 20 per cent. of water the vapour pressure is 1 mm. at 20°, 1·6 mm. at 60°, and 10 mm. at 100°; finally acid containing 2 to 10 per cent. of water shows no vapour pressure of water even at 100°. At concentrations above 98·5 per cent. of H_2SO_4, the pressure is due mainly to vapours of SO_3.[1]

CHEMICAL PROPERTIES. Concentrated sulphuric acid has so great an affinity for water that it abstracts hydrogen and oxygen from many organic

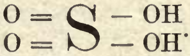
---

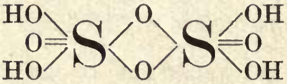
[1] TABLE OF THE VAPOUR PRESSURE OF WATER IN SULPHURIC ACID

Specific gravity of the acid	Per cent. H_2SO_4	TEMPERATURE									
		10°	20°	30°	40°	50°	60°	70°	80°	90°	95°
		Vapour pressure in mm. of mercury									
1·342	44	4·4	8·5	15·5	28·1	48·3	—	—	—	—	—
1·380	48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—	—
1·418	52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9	251·5
1·459	56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0	195·0
1·502	60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7	146·0
1·547	64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7	105·0
1·592	68	0·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0	72·0
1·638	72	0·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7	43·4
1·687	76	0·4	0·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5	22·0
1·733	80	0·2	0·3	0·8	1·3	1·9	2·9	4·1	6·2	9·3	11·0
1·755	82	0·1	0·2	0·5	0·9	1·4	2·0	2·7	3·9	5·6	6·8

substances, and thus chars them. It is used at concentrations above 60° Bé. especially for drying gases. Its vapours are dissociated into SO_3 and H_2O. It decomposes in contact with red-hot porous substances: $SO_4H_2 = H_2O + SO_2 + O$ (p. 195). It does not dissolve platinum, gold, or lead, and when very concentrated does not even attack iron in the cold, and may therefore be transported in tank wagons of sheet iron.[1]

It is a strong acid which displaces other acids from their various salts, but at high temperatures it is displaced in turn by acids which are ordinarily weak but more stable at such temperatures, such as boric, silicic, and phosphoric acids.

In H_2SO_4 hexavalent S is probably present  $\begin{matrix}O= \\ O=\end{matrix}S\begin{matrix}-OH \\ -OH\end{matrix}$. According to G. Oddo and Anelli (1912) the acid in solution would have a doubled molecule, represented perhaps by the structure,



(disulphuric acid); monosulphuric acid does not seem to be known.

It is a dibasic acid forming acid and normal sulphates. Certain normal sulphates, for example, that of copper, redden litmus paper in aqueous solution. The sulphates in general are insoluble in alcohol, and the alkali sulphates remain unaltered even at the highest temperatures, whilst the others decompose, forming metallic oxides $+ SO_2 + O$.

Sulphuric acid is poisonous; magnesia is used as an antidote, but if the acid is concentrated it immediately attacks the mucous membrane of the stomach.

We give on p. 286 a table of densities of sulphuric acid at all concentrations. It should be noted that beyond 65° Bé. (90 per cent. H_2SO_4) it is practically impossible to determine the concentration by means of the density, because this latter varies so slightly; the strength should then be determined by means of direct analysis.

APPLICATIONS OF SULPHURIC ACID. This acid, like soda, is used for such various purposes that the extent of its production is a certain indication of the industrial and civil development of the various nations. About two-thirds of the consumption of chamber acid is used for the production of artificial manures (superphosphates). Further quantities are used in the manufacture of stearine, oleine, and soaps, in the tinning and "galvanising" of iron, in the dyeing of wool and silk, for the production of sodium sulphate, and thus of soda, by the Leblanc process, for the production of hydrochloric

---

[1] *Resistance of metals to the action of H_2SO_4.* Wrought-iron is but slightly resistant in the hot, but in the cold, on the other hand, it is not attacked by acid of greater strength than 60° Bé.; the resistance is greater with iron which contains little silicon, much manganese, much combined carbon, and little graphitic carbon (which is the opposite to the effect produced with regard to the resistance to alkalis). Cast-iron has greater resistance than wrought-iron, even at high temperatures, and is not attacked in the cold by acid of 50° Bé. if air is excluded. For the storage of oleum (fuming acid), on the other hand (*see below*), wrought-iron and not cast-iron vessels must be used. Lead resists dilute acid better than concentrated acid, and the acid in the lead chamber should not exceed a strength of 50° Bé.

Lead is the more resistant the purer it is, and alloys have only a very slight resistance in the hot. Hard lead (which contains 2 to 18 per cent. of antimony) is less resistant on heating. Bismuth renders lead less resistant even if only 0·01 per cent. is present. Concentrated Glover tower acid attacks lead more than concentrated H_2SO_4. Mixtures of concentrated nitric and sulphuric acids, and even concentrated nitric acid (sp. gr. 1·37 to 1·42 alone), attack lead very little in the cold, whilst dilute nitric acid dissolves lead freely even in the cold. Hydrofluoric acid attacks lead slightly at high temperatures (Glover tower); copper resists sulphuric acid better than lead; hard lead is less resistant than pure lead, but develops less hydrogen, and is therefore preferred for the transport of sulphuric acid in closed vessels. Oleum attacks lead more than concentrated H_2SO_4.

and nitric acids, SO_2, CO_2, the sulphates of copper and iron, alum, boot blacking, etc. It is also used in the manufacture of tartaric and citric acids. The more concentrated acid (66° Bé.) is used in the manufacture of nitro-glycerine and various other explosives, of artificial dyestuffs, of petroleum and mineral oils, parchment, paper, etc.

STATISTICS OF PRODUCTION OF H_2SO_4.[1]

In 1905 Germany imported 33,874·6 tons of sulphuric acid at £2 5*s.* per ton, (£76,160), and exported 48,754·5 tons of the value of £109,600. In 1908 the exports rose to 60,000 tons, and the imports also rose. In 1909 the exports were 64,000 tons and the imports 74,400 tons; in 1913 the imports exceeded the exports by 65,300 tons.

In 1905 the United States produced 94,000 tons of sulphuric acid from zinc sulphide, and in 1911 about 200,000 tons, besides 200,000 tons from sulphur dioxide recovered from the furnaces in which copper ores were treated (*see* chapter on Copper). In 1908 there were 15 works which used crude sulphur, with a yield of 432 per cent. of sulphuric acid at 50° Bé., and 105 works which worked with iron pyrites, with a yield of 211 per cent.

						£
In Italy in	1879	13	works produced	10,000	tons at 52° Bé., value	45,720
,,	1890	20	,,	60,000	,, ,,	120,000
,,	1901	30	,,	235,000	,, ,,	357,600
,,	1903	—	,,	263,018	,, ,,	397,868
,,	1905	—	,,	302,100	,, ,,	400,908
,,	1908	90	,,	524,210	,, ,,	840,000
,,	1910	—	,,	550,000	,, ,,	860,000
,,	1911	—	,,	400,000	,, ,,	640,000
,,	1912	110	,,	545,000	,, ,,	840,000
,,	1914	—	,,	630,000	,, ,,	926,800

About 80 per cent. of all the sulphuric acid produced in Italy is used in manure factories, the larger number of which are connected with the sulphuric acid factories. Six per cent. is used for copper sulphate, 3½ per cent. for the manufacture of nitric and hydrochloric acids, 4½ per cent. in the preparation of sulphates of aluminium, ammonium, manganese, barium, zinc, etc., and 6½ per cent. for all other purposes. In 1908 Italy exported 200 tons of sulphuric acid valued at £600. For the manufacture of superphosphates England in 1911 consumed about 1,000,000 tons of sulphuric acid at 60° Bé., Germany 1,400,000 tons, and France 1,600,000 tons.

In 1880 the world's production was 1,850,000 tons, in 1890 2,818,000 tons, in 1902 4,450,000 tons, in 1909 8,000,000 tons (calculated at 60° Bé.), in 1910 about 5,000,000 tons (100 per cent.) and in 1913 about 5,500,000 tons.

---

[1] The production of sulphuric acid in different countries during a period of thirty-five years is shown in the following table, the figures denoting thousands of tons of 100 % acid.

Year	Whole World	Great Britain	Germany	France	Italy	Belgium	Austria	Russia	United States	Japan
1878	650	—	—	—	7	—	—	—	—	—
1880	1400	—	190	—	—	—	—	—	—	—
1885	—	—	—	—	—	—	—	—	—	—
1890	—	650	—	200	40	—	—	—	500	—
1895	—	—	500	—	—	—	—	—	—	—
1900	3000	759	800	500	145	105	130	82	700	16
1902	3500	—	—	—	165	—	—	—	—	—
1904	4100	1100	900	600	180	165	200	125	950	50
1906	—	1100	—	700	237	—	—	—	—	52
1908	—	—	1200	780	340	—	—	165	1200	120
1910	—	1000	1300	875	418	—	—	—	1400	—
1911	5400	1000	1500	—	388	—	—	—	1500	—
1912	—	—	1650	—	415	—	—	—	—	—
1913	5500	—	—	—	419	250	—	—	—	—

SPECIFIC GRAVITIES OF SULPHURIC ACID SOLUTIONS AT 15° C. (LUNGE).

Sp. gr. at $\frac{15°}{4}$ (vacuum)	Baumé degrees	100 parts by weight of pure acid contain—		1 litre of pure acid contains in kilos		Sp. gr. at $\frac{15°}{4}$ (vacuum)	Baumé degrees	100 parts by weight of pure acid contain—		1 litre of pure acid contains in kilos	
		SO_3	SO_4H_2	SO_3	SO_4H_2			SO_3	SO_4H_2	SO_3	SO_4H_2
1·005	0·7	0·68	0·83	0·007	0·008	1·495	47·8	48·34	59·22	0·723	0·885
1·015	2·1	1·88	2·30	0·019	0·023	1·505	48·4	49·12	60·18	0·739	0·906
1·025	3·4	3·07	3·76	0·032	0·039	1·515	49·0	49·89	61·12	0·756	0·926
1·035	4·7	4·27	5·23	0·044	0·054	1·525	49·7	50·66	62·06	0·773	0·946
1·045	6·0	5·45	6·67	0·057	0·071	1·535	50·3	51·43	63·00	0·789	0·967
1·055	7·4	6·59	8·07	0·070	0·085	1·545	50·9	52·12	63·85	0·805	0·987
1·065	8·7	7·73	9·47	0·082	0·102	1·555	51·5	52·79	64·67	0·821	1·006
1·075	10·0	8·90	10·90	0·096	0·117	1·565	52·1	53·46	65·49	0·837	1·025
1·085	11·2	10·04	12·30	0·109	0·133	1·575	52·7	54·13	66·30	0·853	1·044
1·095	12·4	11·16	13·67	0·122	0·150	1·585	53·3	54·80	67·13	0·869	1·064
1·105	13·6	12·27	15·03	0·136	0·166	1·595	53·9	55·55	68·05	0·886	1·085
1·115	14·9	13·36	16·36	0·149	0·183	1·605	54·4	56·30	68·97	0·904	1·107
1·125	16·0	14·42	17·66	0·162	0·199	1·615	55·0	57·05	69·89	0·921	1·128
1·135	17·1	15·48	18·96	0·176	0·215	1·625	55·5	57·75	70·74	0·938	1·150
1·145	18·3	16·54	20·26	0·189	0·231	1·635	56·0	58·43	71·57	0·955	1·170
1·155	19·3	17·59	21·55	0·203	0·248	1·645	56·6	59·10	72·40	0·972	1·192
1·165	20·3	18·64	22·83	0·217	0·266	1·655	57·1	59·78	73·23	0·989	1·212
1·175	21·3	19·69	24·12	0·231	0·283	1·665	57·7	60·46	74·07	1·007	1·233
1·185	22·5	20·73	25·40	0·246	0·301	1·675	58·2	61·20	74·97	1·025	1·256
1·195	23·5	21·78	26·68	0·260	0·319	1·685	58·7	61·93	75·86	1·043	1·278
1·205	24·5	22·82	27·95	0·275	0·337	1·695	59·2	62·64	76·73	1·062	1·301
1·215	25·5	23·84	29·21	0·290	0·355	1·705	59·7	63·35	77·60	1·080	1·323
1·225	26·4	24·88	30·48	0·305	0·373	1·715	60·2	64·07	78·48	1·099	1·346
1·235	27·4	25·88	31·70	0·320	0·391	1·725	60·6	64·78	79·36	1·118	1·369
1·245	28·4	26·83	32·86	0·334	0·409	1·735	61·1	65·50	80·24	1·136	1·392
1·255	29·3	27·76	34·00	0·348	0·426	1·745	61·6	66·22	81·12	1·156	1·416
1·265	30·2	28·69	35·14	0·363	0·444	1·755	62·1	66·94	82·00	1·175	1·439
1·275	31·1	29·62	36·29	0·377	0·462	1·765	62·5	67·65	82·88	1·194	1·463
1·285	32·0	30·57	37·45	0·393	0·481	1·775	63·0	68·49	83·90	1·216	1·489
1·295	32·8	31·52	38·61	0·408	0·500	1·785	63·5	69·47	85·10	1·240	1·519
1·305	33·7	32·46	39·77	0·424	0·519	1·795	64·0	70·45	86·30	1·265	1·549
1·315	34·6	33·41	40·93	0·439	0·538	1·805	64·4	71·50	87·60	1·291	1·581
1·325	35·4	34·35	42·08	0·455	0·557	1·815	64·8	72·69	89·05	1·319	1·621
1·335	36·2	35·27	43·20	0·471	0·577	1·821	65·0	73·63	90·20	1·341	1·643
1·345	37·0	36·14	44·28	0·486	0·596	1·823	65·1	73·96	90·60	1·348	1·651
1·355	37·8	37·02	45·35	0·502	0·614	1·825	65·2	74·29	91·00	1·356	1·661
1·365	38·6	37·89	46·41	0·517	0·633	1·827	65·3	74·69	91·50	1·364	1·671
1·375	39·4	38·75	47·47	0·533	0·653	1·829	65·4	75·03	91·90	1·372	1·681
1·385	40·1	39·62	48·53	0·549	0·672	1·831	65·5	75·35	92·30	1·380	1·690
1·395	40·8	40·48	49·59	0·564	0·692	1·833	65·6	75·72	92·75	1·388	1·700
1·405	41·6	41·33	50·63	0·581	0·711	1·835	65·7	76·27	93·43	1·400	1·713
1·415	42·3	42·17	51·66	0·597	0·730	1·837	65·7	76·90	94·20	1·412	1·730
1·425	43·1	42·96	52·63	0·612	0·750	1·839	65·8	77·55	95·00	1·426	1·748
1·435	43·8	43·75	53·59	0·628	0·769	1·840	65·9	78·04	95·60	1·436	1·759
1·445	44·4	44·53	54·55	0·643	0·789	1·8415	—	79·76	97·70	1·469	1·799
1·455	45·1	45·31	55·50	0·659	0·808	1·8405	—	80·57	98·70	1·483	1·816
1·465	45·8	46·07	56·43	0·675	0·827	1·8395	—	81·18	99·45	1·494	1·830
1·475	46·4	46·83	57·37	0·691	0·846	1·8385	—	81·59	99·95	1·500	1·838
1·485	47·1	47·57	58·28	0·707	0·865						

The consumption of concentrated sulphuric acid for the manufacture of explosives alone is enormous and has been calculated indirectly to be roughly as follows (tons):

	Italy	France	England	U.S.	Austria	Germany
1915	60,000	600,000	480,000	400,000	350,000	1,400,000
1916	180,000	1,200,000	800,000	600,000	600,000	2,000,000

The price of sulphuric acid varies somewhat; crude lead chamber acid at 52° Bé. is sold at about £1 8*s.* per ton; that at 60° Bé. at about £2 8*s.* per ton, at 65° to 66° Bé. up to £3 4*s.* per ton for small amounts. During the European war large quantities have been sold in Italy for £4 16*s.* to £5 12*s.* per ton.

PREPARATION OF H_2SO_4. The formation of this acid by decomposition of certain metallic sulphates is of theoretical interest:

$$Ag_2SO_4 + 2HCl = 2AgCl + H_2SO_4.$$
$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

H_2SO_4 was first prepared on a large scale by heating ferrous sulphate and condensing the gas in a little water, thus using the sulphur trioxide only: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$.

Attempts were also made to obtain it by the interaction of chlorine, SO_2, and water, as was explained on p. 178. In 1910 A. Coehn and H. Becker investigated the reaction $SO_2 + O \rightarrow SO_3$ under the influence of ultra-violet rays (from a mercury vapour lamp) but without a catalyst, and at temperatures between 160° and 800°. They found that, in the dark, the transformation into SO_3 takes place to the extent of 100 per cent., but at 800° of only 30 per cent. The preparation of H_2SO_4 by passing the mixture of H_2S and SO_2 (as obtained in the recovery of sulphur in Leblanc soda works by the Chancel-Claus process, *see* Part III) over a catalytic mass of platinum at 540° has also been proposed (Ger. Pat. 157,589). In 1909 H. Trey (Ger. Pat. 207,761) obtained sulphuric acid by heating calcium sulphate with silicious sand to 1250° to 1400°; the sand contained 0·5 per cent. of iron oxide, which acts as a catalyst. The mixture of $SO_2 + O$ which is formed may also be used for the catalytic preparation of SO_3 (*see below*); the silicious residue from this process may be utilised in glass factories. This process has already been applied in a large works. According to a United States patent (930,471 of 1909) by W. Hallock, sulphuric acid is obtained by submitting a mixture of $SO_2 + H_2O$ + air to the action of radio-active emanations.

Sulphuric acid is now prepared industrially from SO_2 obtained by burning iron, copper, or zinc pyrites (the copper and zinc are then utilised, as explained in Part III, Copper Sulphate, etc.).

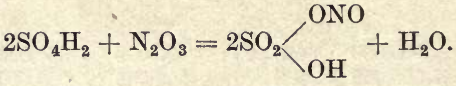
$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2 + 419{\cdot}8 \text{ cals.}$$

When this reaction has been once started further heat is no longer required, because sufficient heat is evolved during combustion to continue the burning of the pyrites.

The gas which is produced by burning the pyrites in suitable burners (*see below*) contains 7 to 8 per cent. of SO_2, the remainder being air and excess of nitrogen. Steam and oxygen (furnished by nitrous fumes) are added to this gas and the formation of H_2SO_4 takes place in large leaden chambers (*see below*).

The phenomena which occur in the lead chambers have been the subject of a great deal of work and of many interpretations, as will be noted later.

The nitrogen of the air and the excess of air, when they issue from the lead chamber, carry with them considerable quantities of N_2O_3 (red vapours) which are utilised by absorbing them with concentrated sulphuric acid in the Gay-Lussac towers. The so-called "nitrous" acid, which is a solution of nitrosylsulphuric acid (also called Weber's acid) in sulphuric acid, is thus obtained:



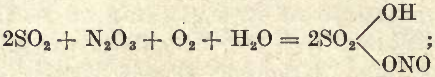
$$2SO_4H_2 + N_2O_3 = 2SO_2\left\langle\begin{array}{l}ONO\\ OH\end{array}\right. + H_2O.$$

The nitrogen oxides are recovered from this acid in the Glover tower, through which the current of SO_2 from the burners is passed (*see below*).

The sulphuric acid which collects on the floor of the lead chamber contains about 63 to 65 per cent. of H_2SO_4. We shall explain later how this is concentrated when necessary.

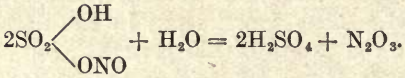
THEORY OF THE FORMATION OF H_2SO_4 IN THE LEAD CHAMBER. In 1884–1885 Lunge and Naef[1] showed experimentally, by analysing the gases in the lead chamber of a large works, that in the first chamber excess of NO is present compared with the NO_2, and that the gases are only slightly coloured; in the succeeding chambers about equal quantities of NO and NO_2 are always present. Neither in any of the chambers nor in the acid formed was excess of NO_2 present, nor was nitric acid found, and thus they believe that the reaction is caused not by the peroxide N_2O_4, but always by the trioxide N_2O_3, with intermediate formation of crystals of nitrosylsulphuric acid, which, with steam, give H_2SO_4, regenerating N_2O_3:

(1)



$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\left\langle\begin{array}{l}OH\\ ONO\end{array}\right. ;$$

(2)



$$2SO_2\left\langle\begin{array}{l}OH\\ ONO\end{array}\right. + H_2O = 2H_2SO_4 + N_2O_3.$$

In order to explain why the excess of NO is present in the first chamber where the reaction is more energetic and the temperature higher, Lunge suggested later that a direct action also occurs between nitrosylsulphuric acid and SO_2, an excess of NO being thus generated according to the equation:

$$(3)\qquad 2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3SO_4H_2 + 2NO.$$

He supposed that the nitric oxide thus formed in its turn renders the process in the first chamber more active by transforming SO_2 directly into nitrosylsulphuric acid, with the help of air and water vapour:

$$(4)\qquad 2SO_2 + 2NO + 3O + H_2O = 2SO_2(OH)(ONO).$$

The reactions which occur in the lead chamber are in part reversible, and in order to explain them according to the mass law, it is necessary that there should be certain rela-

---

[1] A theory had already been propounded by Clément and Désormes in 1806, and developed by Davy in 1812, which supposed the following reactions to occur: $2SO_2 + 3NO_2 + H_2O = NO + 2SO_2(OH)(ONO)$ (chamber crystals). The NO is transformed into NO_2 by the oxygen of the air, and the crystals form H_2SO_4 with steam and air, regenerating nitrogen peroxide: $2SO_2(OH)(ONO) + H_2O + O = 2SO_4H_2 + 2NO_2$. This theory was partially upheld later by Gmeling (1852), Winkler (1867), and Lunge (1884–1903), with certain modifications concerning the formation of nitrosylsulphuric acid.

In 1835 and 1844 Berzelius, who was followed by many other chemists during the next few years, maintained that the formation of crystals was not necessary and that the reaction occurred by the direct interaction of nitrogen peroxide (NO_2 or N_2O_4), SO_2 and water: $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$, and that the NO reacted with the oxygen of the air to re-form NO_2. He supposed confusedly that a mixture of N_2O_3 and N_2O_4 was present in the chamber and gave rise to the formation of sulphuric acid. Peligot also, in 1844, did not admit that crystals were formed, and attributed the oxidation of the SO_2 to the direct action of nitric acid and of regenerated nitrogen peroxide, which with water again formed nitric acid: $SO_2 + 2NO_3H = SO_4H_2 + N_2O_4$.

In 1867 R. Weber showed that the theory of Peligot was untenable because HNO_3 in contact with SO_2 forms H_2SO_4 slowly, whilst the reaction is easy with nitrous acid (HNO_2 or N_2O_3), especially if this is dissolved in water or dilute H_2SO_4, even without the formation of crystals: $SO_2 + N_2O_3 + H_2O = 2NO + H_2SO_4$. In 1867 C. Winkler maintained, on the other hand, that the nitric oxide formed in the reaction is transformed into NO_2 or N_2O_4 by the oxygen of the air, and that this forms a white cloud of crystals of nitrosylsulphuric acid in contact with SO_2 and water vapour. This cloud is deposited, and in contact with the hot dilute sulphuric acid of the chamber decomposes into H_2SO_4 and NO, which latter is evolved as gas and again takes part in the cycle of reactions.

tions between the reacting substances in order that the reaction may proceed in a given sense. Thus, if air or nitrous vapours are present in abundance the reactions (1) and (4) preponderate, whilst if there is a relative excess of SO_2 the reaction (3) will preponderate, and the gases are lighter in colour through the formation of colourless NO. This does not matter in the first chamber because NO is able to give the reaction (4), but it is harmful if it occurs in the last chamber, and NO is then lost, as it is not absorbed by H_2SO_4 in the Gay-Lussac tower. N_2O_3 should, therefore, abound in the last chamber [reaction (1)], so that all the SO_2 may be utilised. The vapours in the last chamber should be strongly yellowish brown in colour (N_2O_3). In general, then, the process in the chambers is regular and good if oxygen and nitrous vapours are abundant; otherwise SO_2 is lost, and if excess of air only be present this alone is incapable of oxidising SO_2 and transforming it into H_2SO_4. During normal working not more than 0·5 per cent. of the sulphur burned in the furnaces should be present in the final gases in the state of SO_2.

The equilibrium between the various reactions in the interior of the lead chambers is very complex, and depends on three principal factors, that is, on the quantitative relations between the reacting substances, the temperature and the volume of the lead chamber. The formation and decomposition of nitrosylsulphuric acid are closely connected with the vapour pressure inside the chamber, and thus depend on the temperature and on the concentration of the sulphuric acid in the chamber itself, as well as on that of the condensed liquid, which is suspended in droplets like a cloud. It must be remembered that the solution of N_2O_3 in H_2SO_4 (nitrosylsulphuric acid) has a less vapour pressure and is therefore the more stable, the greater the concentration of the acid and the lower the temperature, whilst the pressure of the N_2O_3 increases with dilution of the acid, that is, by the action of water, and with elevation of the temperature, that is, the nitrosylsulphuric acid then regenerates N_2O_3 and H_2SO_4. In order to deduce *a priori* the state of affairs in the lead chamber, it is necessary to consider the temperature, the concentration of the acid which collects in the chamber, the quantity of water vapour, etc.

Lunge, Hurter, and Sorel have been able to demonstrate experimentally that in the lead chamber the process of sulphuric acid formation corresponds very well with that theoretically derived from the pressure of H_2SO_4 vapours (in liquid or in drops).

Of late years it has been found that the so-called blue acid, H_2SNO_5 (sulphonitronic acid, discovered by Sabatier), may be formed in Gay-Lussac towers when an excess of nitrosylsulphuric acid has been formed or when the temperature is higher than 30°, in presence of the coke which fills the tower. This acid decomposes to form sulphuric acid with loss of NO. Raschig maintains that this acid is always formed as an intermediate product in the production of sulphuric acid, and Lunge assumed in 1907 that the reaction (1) occurs in two phases: (1*a*) $SO_2 + NO_2 + H_2O = H_2SNO_5$, and (1*b*) $2H_2SNO_5 + O = H_2O + 2HSNO_5$ (nitrosylsulphuric acid), and that the reaction (3) also occurs in two phases: (3*a*) $2HSNO_5 + SO_2 + 2H_2O = H_2SO_4 + 2H_2SNO_5$, and (3*b*) $H_2SNO_5 = H_2SO_4 + NO$, the cycle of reactions which forms sulphuric acid being then completed by reaction (4*a*) $2NO + O_2 = 2NO_2$, which re-enters into reaction (1*a*).

In 1895 and 1901 Ostwald endeavoured to explain the formation of sulphuric acid in the lead chamber by attributing it to the catalytic action of N_2O_3, which, without taking any part in the reaction, was able, he supposed, to increase the velocity of the reaction, $SO_2 + O + H_2O = SO_4H_2$, this being under ordinary conditions, very slow and almost imperceptible. In 1903, however, Lunge maintained that one cannot speak of a catalyst when the formation of intermediate products and the very great facility of reaction of these products without the intervention of the catalyst have been demonstrated.

In the case of true catalytic actions there are no intermediate reactions, and the catalyst merely accelerates reactions which would take place very slowly without it, though in some cases they need several years in order to become apparent (*see* p. 70). It is maintained by some that H_2SO_4 is formed in the chamber only in contact with the leaden walls, which would thus act as catalysts, and hence the tendency to increase the surface area, as, for example, in Gilchrist's process.

The theoretical interpretation of the reactions taking place in the lead chamber is continuously under discussion, and the polemics have not yet terminated, but are being energetically carried on with abundance of theoretical arguments and experimental results by Lunge, Raschig, and others.

In 1904 to 1908 Raschig attributed to the crystals of the lead chamber the constitutional formula SO_2 (OH) (NO_2) (nitrosulphonic acid), but he also supposed the intermediate formation in the chamber of nitrososulphuric acid, $HSNO_4$ (thus $HNO_2 + SO_2 = HSNO_4$), which, with HNO_2, forms blue acid, H_2SNO_5.

In 1904 Trautz, on the other hand, combined the various reactions of Lunge and Raschig, and arrived at the following inclusive equation: $SO_2 + 2NO + O + H_2O = H_2SO_4 + 2NO$, that is to say, he supposed that NO acts as a catalyst only, without taking part in the reaction.

From 1893 to 1910 Jurisch maintained that the reactions of Lunge and Raschig take place only when the lead chamber is behaving abnormally (that is, when there is excess or deficiency of steam, air, or nitrous products, etc.). In the complete absence of water even nitrogen may be formed: $3SO_2 + N_2O_3 = 3SO_3 + N_2$, whilst during normal working the presence of N_2O_3 suffices to explain the continuous formation of sulphuric acid by means of a catalytic action or by continuous regeneration from NO and the atmospheric oxygen.

INDUSTRIAL PREPARATION OF SULPHURIC ACID

This industry has to-day acquired an extraordinary importance in every country, serving as the basis of many other industries, and the development of sulphuric acid manufacture is justly used as a measure of the industrial progress of a nation. For this reason we shall enter into various details in describing the most important operations and processes of this industry, which is very extensive in Italy.[1]

---

[1] The first sulphuric acid works were erected by Ward in 1740 at Richmond, near London. He heated a mixture of sulphur and saltpetre in iron capsules and collected the sulphuric acid vapours in glass vessels of 300 litres capacity, containing a little water. The product was concentrated by heating the glass vessels in a sand-bath, but great inconvenience was caused by the ease with which the vessels were broken. In order to avoid this trouble, Roebuck and Garbett in 1746 replaced them by receptacles or chambers of lead about two metres wide, inside which a central furnace produced the acid from sulphur and saltpetre. In 1766 this method was first introduced into France by Holker (at Rouen); in 1774 La Follie also passed a jet of steam into the lead chamber, and in 1793 Clément and Désormes showed the importance in the lead chamber of a current of air, which facilitated the formation of sulphuric acid and effected a notable saving of nitre and sulphur. Thus, before that time only 130 kilos of sulphuric acid were obtained from 100 kilos of sulphur, whereas to-day this yield is more than doubled. They had then already correctly interpreted the process of sulphuric acid formation, and they stated that the nitric acid was merely a means of fixing (by nitrous vapours) the atmospheric oxygen, which transformed the SO_2 into SO_3. In 1835 the first Gay-Lussac towers were installed in France for the condensation of nitrous vapours, and these effected a great economy of saltpetre.

In 1861 the first Glover tower was erected (at Newcastle) in order to regenerate the nitrous vapours condensed by sulphuric acid in the Gay-Lussac tower. Until about the year 1835 Sicilian sulphur had always been employed for the manufacture of sulphuric acid, but when the Government of Ferdinand II. of Bourbon, at Naples in 1858, conceded the monopoly of sulphur-mining to the firm of Taix-Aycard and Co., of Marseilles, a concession which raised the price from 9*s*. 7*d*. to 28*s*. per 100 kilos, all Europe endeavoured to obtain sulphur from other sources, especially from pyrites; America alone used impure Sicilian sulphur, containing 90 per cent. of sulphur, until 1882. In 1835 Perret had already devised a furnace for roasting pyrites and obtaining the sulphur in the form of SO_2, and in 1852 Usiglio proposed the use of muffle-furnaces, which, however, left a residue containing 15 per cent. of sulphur. From 1848 to 1867 the furnaces were further perfected by Perret and then by Olivier, who constructed the burners with several grates in order to burn lumps of pyrites as well as more finely divided product.

The first sulphuric works in Italy were constructed in 1805 and enlarged in 1815 in the church

Very little pure sulphur is to-day employed as the source of sulphuric acid. The sulphur obtained in the purification of lighting gas, which contains it as H_2S, is sometimes used, as also is that regenerated from the residues of the Leblanc soda industry. During the last few years Oddo has proposed the use of sulphur ores directly, but on account of certain technical difficulties and for economic reasons it does not appear to be practicable. Almost all sulphuric acid is to-day obtained from pyrites.

PYRITES. Pyrites is the material which is to far the greatest extent used to-day, especially iron pyrites, FeS_2, which contains 42 to 50 per cent. (theoretically 53·33 per cent.) of sulphur. This is found abundantly in large mineral deposits in various countries, and often contains admixtures of sulphides of lead, zinc, copper, etc. In such cases, the copper, lead, zinc, gold, nickel, selenium, tellurium, thallium, etc., which it may contain, are also utilised and the sulphur is thus obtained at a lower cost.

Pyrites is most abundant in Spain, in which country there are deposits 107 kilometres long and 30 kilometres broad; at some points their depth reaches 40 metres and they contain about 50 per cent. of sulphur (*see* section, Iron Sulphide).

In Italy the most important deposits of pyrites are in the Val d'Aosta, containing 48 to 50 per cent. of sulphur and much arsenic (about 1 per cent., whilst the pyrites of Brosso contains a maximum of 0·2 per cent.). There are also important mines in Libiola, near Genoa, in Bergamasco, with about 0·5 per cent. of As; in Venetia (Agorda and Vicenza), in Pallanza (30 to 35 per cent. of sulphur and up to 1 per cent. of nickel), in the Island of Elba, in Traversella, etc.; pyrites containing a considerable amount of copper is found in certain Tuscan mines. Pyrites containing less than 30 per cent. of sulphur burns badly. The consumption of pyrites for sulphuric acid manufacture in Italy in 1893 was about 60,000 tons, whilst the consumption of sulphur for the same purpose was 1000 tons. In 1908 Italy produced 132,000 tons of pyrites, and imported 164,400 tons, of which about half came from Spain and part from Cassandra.[1] The Italian output of pyrites is now greatly increased, especially in Tuscany (Montecatini pyrites), and a considerable quantity is exported. Pyrites is bought according to the percentage of sulphur, and for each unit of sulphur 3·7*d.* to 5·3*d.* is paid per ton. Pyrites containing 50 per cent. of sulphur at 4·8*d.* per unit thus costs £1 per ton at Genoa (customs charges not included).

The sulphur contained in pyrites as copper sulphide is not much utilised, because it partially forms calcium sulphate with calcium carbonate. That contained as zinc sulphide was formerly utilised to only one-half its extent, but it is utilised more completely at the present time.

When 100 kilos of pyrites are burned 70 to 73 kilos of ash are obtained, which consists almost entirely of ferric oxide, Fe_2O_3 (*burnt pyrites*).[2]

---

of San Vincenzo al Prato in Milan, conceded freely by Napoleon to Francesco Fornara di Massimo d'Arona. The Sclopis works at Turin were erected about the year 1845 with lead chambers (though for many years these works produced H_2SO_4 without chambers), and a few years afterwards the important works of Candiani and Biffi at Milan were erected.

[1] During the Turko-Italian War in 1911–1912, Greek pyrites (Cassandra) could not be imported (into Italy), and the price rose in 1912 to 7·5*d.* per ton-unit. During the European War (at the end of 1916) pyrites reached the price 11·5*d.* per ton-unit; with these prices, sulphur or sulphur ores can be used in place of pyrites.

[2] The utilisation of burnt pyrites is a problem which has not been solved, and in many cases the works are more or less choked by the enormous accumulated masses of this by-product (1 cu. metre weighs 1·6 to 1·7 tons). In 1874 Hochberger advised the use of burnt pyrites, after sifting, for the polishing of glass and mirrors, and it has been used for this purpose, but the consumption is absurdly small. It is used also as road metal, but then gives very much dust. It is employed for absorbing H_2S in gas manufacture, but is not so suitable for this purpose as limonite, and requires larger plant than the latter. Buisine uses it for the preparation of sulphur, ferrous sulphate and ferric sulphate, by heating it with acid at 60° Bé. Attempts have also been made to manufacture bricks from burnt pyrites. Arnois obtained a red mineral pigment similar to colcothar by mixing it with 3 to 4 per cent. of NaCl and $CaCO_3$ and heating to redness in an oxidising furnace. Pyrites burnt in lumps still contains 1·5 to 3 per cent. of sulphur, and burnt powdered pyrites from 0·7 to 1·5 per cent. Cupriferous pyrites contains 1·5 to 4 per cent. of sulphur after burning, this being present partly as sulphide and partly as sulphate. A considerable quantity of burnt pyrites, containing comparatively little sulphur, is utilised in large metallurgical centres for the preparation of iron in blast-furnaces. It does not stand heavy freight charges, and therefore in certain centres where large quantities of burnt pyrites are obtained it may, perhaps, pay to erect a small blast-furnace for the production of iron of poor quality, which has, however, only a low value.

Burnt pyrites is also used in electric furnaces to produce cast-iron and steel, but not always successfully. In order that it may be utilised for the manufacture of these products, burnt

Pyrites containing copper is more valuable, but it is necessary to roast it only to such a point that the copper still remains in the form of sulphide, because it is thus more easily extracted. Lead, zinc, and calcium carbonate are disadvantageous in iron pyrites because they form undecomposable sulphates on roasting. Calcium fluoride produces HF, which damages stoneware and lead apparatus. If the pyrites contains arsenic, arsenic trioxide is formed; this is sometimes harmful, and the acid of the first chamber may contain up to 0·2 per cent. of As, and that from the Glover tower up to 0·35 per cent. Pyrites which is poor in sulphur gives a smaller *relative* yield, and the cost of working is proportionately greater for the same quantity of sulphur than in the case of rich pyrites.[1]

PYRITES BURNERS. The first burners were those of Olivier-Perret, which worked badly on account of the varying size of the crushed pyrites. In the works of Maletra at Rouen and at St. Denis, separate burners are constructed for roasting pyrites in lumps and in powder. These Maletra furnaces are in general use to-day, with various modifications in all works.

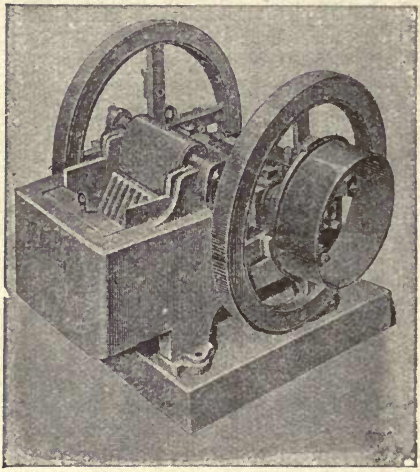


FIG. 100.

The pyrites first passes through a rock-breaker (Fig. 100) which is able to treat 40 to 130 tons of pyrites in ten hours; 86 per cent. of the product consists of pieces as large as nuts and 14 per cent. of small pieces and powder.

The ore is charged into the rock-breaker on the left and falls on to the grooves of a hard cast-iron plate, to which a vertical oscillatory movement is imparted by means of large flywheels, and a sort of mastication of the mineral is thus effected.

---

pyrites should contain less than 11 per cent. SiO_2, 0·5 per cent. Pb, 0·3 per cent. Cu, 0·03 per cent. As, 0·04 per cent. P, 3 per cent. S, 0·5 per cent. Zn, and 0·5 per cent. Ca, and at least 58 per cent. Fe. Prior to the European War, Italy exported burnt pyrites at a price of less than 10*d.* per ton where produced, freight charges being paid by the purchaser; it was shipped from Genoa to Germany, Belgium, and England. The great Creuzot works in France brings burnt pyrites overland from a distance of 400 kilometres and mixes it to the extent of 20 to 25 per cent. with iron ores in the blast furnaces.

[1] The production (pr.) and consumption of pyrites are shown by the following figures; imp. indicates importation and the numbers represent tons.

		1900	1905	1909	1910	1911	1912	1913	1914
Spain	export.	—	—	—	1,350,000	—	2,991,200	2,904,000	—
	pr.	34,638	179,100	250,000	—	—	—	—	—
France .	pr.	305,000	267,100	286,000	300,000	—	—	—	—
	imp.	156,800	271,690	360,000	350,000	—	—	—	—
Germany .	pr.	169,450	185,370	193,000	215,700	217,460	110,000	—	—
	imp.	457,680	552,180	691,000	793,000	862,200	1,076,500	1,027,000	—
Austria-Hungary and Bosnia	pr.	89,000	126,000	—	—	—	—	—	—
Italy . .	pr.	72,000	117,700	149,000	171,000	166,000	277,000	318,000	—
	imp.	23,000	100,000	150,600	115,800	103,900	70,707	40,512	27,250
U.S. . . .	pr.	204,600	228,580	249,000	244,000	303,000	356,000	347,000	340,000
	imp.	326,000	521,000	695,000	811,000	1,016,000	971,000	864,000	1,045,000
Canada .	pr.	36,300	29,700	57,000	—	—	80,000	—	—
	imp.	—	—	—	—	—	—	—	—
Russia .	pr.	23,000	30,700	—	59,000	—	—	—	—
	imp.	—	—	90,000	115,000	—	—	—	—
Norway .	pr.	98,950	162,000	162,000	—	350,000	430,000	460,000	—
	export.	—	—	—	—	—	—	390,000	—
England .	pr.	12,500	12,500	12,300	8,429	9,400	10,522	11,400	11,650
	imp.	—	740,000	699,000	790,900	812,000	—	—	—
Portugal .	pr.	402,870	352,480	352,500	400,000	—	—	—	—
Japan .	pr.	16,170	25,570	28,000	40,000	—	—	—	—

The world's consumption of pyrites was 300,000 tons in 1860, 2,000,000 tons in 1905, and 3,200,000 tons in 1910. In 1915–1916, during the European War, Germany was unable to import pyrites owing to the blockade, and the other countries increased their consumption for the production of explosives.

(*a*) **Pyrites Burners for Lumps.** The furnaces are constructed of brickwork and the floor is formed of a grate of rotatable bars on which the lumps of pyrites are distributed. The relationship between the surface of the grate, the height of the layer of pyrites, and the quantity which can be burned in twenty-four hours, has to be determined for any given quality of ore. A furnace which was employed with satisfactory results in Muspratt's works is constructed with a grate containing fifteen rotatable bars of square cross-section arranged in such a manner that their corners are opposite to one another : (◇◇); these occupy a surface of about 2 sq. metres. They are charged with a layer of pyrites 60 cm. deep, and 450 kilos are burned per twenty-four hours, the residue containing 2 per cent. of S.

As many as twelve double furnaces are arranged in one row, so that there are twenty-four furnaces in all, and these are charged every twelve hours, the mass being lighted from above by means of two pieces of red-hot coke. Before recharging the furnace the residue of burnt pyrites and ash is made to fall by turning the square bars in such a way that the intervals are enlarged (□ □).

In order to avoid fusion of the ash in the case of rich pyrites, a smaller amount is charged into the furnace. The temperature of the gas which leaves the ovens varies between 400° and 500°. The supply of air is regulated by a sliding damper which is placed under the grate.

(*b*) **Furnaces for Pyrites Powder.** Maletra furnaces, which were shown in 1873 at the International Exhibition in Vienna, are ordinarily used.

They consist of double furnaces placed back to back and joined to one another, each being formed of six hearths of fireclay 6 to 7 cms. thick, connected with one another and supported in the middle in such a way that the six hearths are each about 3 metres long and about 80 cms. wide (Fig. 101).

In twenty-four hours 30 kilos of pyrites can be burned per square metre of surface.

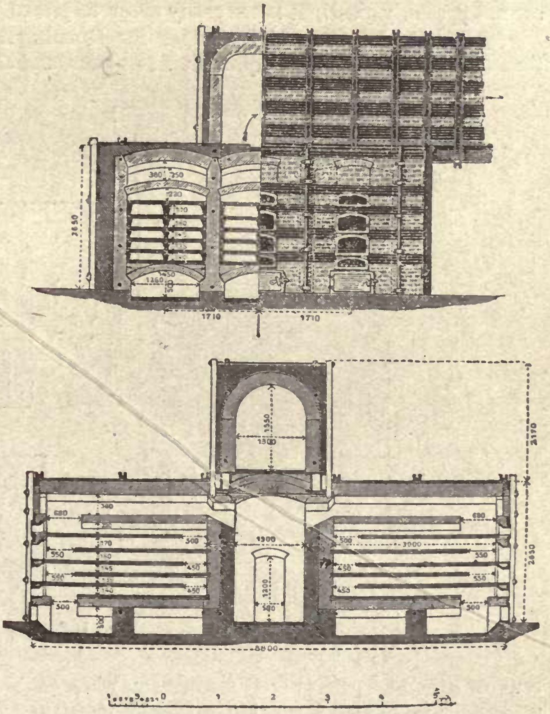


FIG. 101.

When the furnace is new it must be heated to a dark red heat for the first time very slowly and with very great precautions, by means of a separate hearth, which is then bricked up when the furnace has reached the necessary temperature. During this interval the furnace gases pass out through the chimney, but when the pyrites commences to burn, the communication with the chimney is closed and the gases are then turned into the Glover tower. The first charge is composed of thin layers of powdered pyrites on each alternate hearth, and the partially roasted pyrites is made to pass gradually, by means of suitable tools, from the hearth above to the next hearth below, the upper hearth being then again charged. The exhausted and well-burnt residue finally arrives at the lowest hearth and contains only 1½ to 3 per cent. of sulphur, whilst in the first furnaces as much as 10 per cent. of the sulphur was lost. The burnt pyrites finally falls into the cooling-box or directly into small iron wagons placed below, and are then removed.

When regular working is established the upper hearth of each furnace is charged with 150 kilos of pyrites, and each furnace burns 600 kilos per twenty-four hours. The sulphurous gases leave the furnace at a temperature of about 400° and first pass into large flues or chambers, where the dust carried over is almost completely deposited. These dust chambers are so constructed that the gases are forced to pursue a zigzag path by means of transverse walls, and if the pyrites contains much arsenic the gases must also be passed through very long wide flues, where the As_2O_3 is deposited.

In Germany, where zinc blende is very abundant, special large muffle-furnaces are constructed in order to utilise the sulphur which it contains.

If molten slag is formed on the hearth, it must be removed immediately from the furnace, as otherwise it increases in quantity and causes loss of sulphur (up to 10 per cent).

The gases which are formed in these pyrites burners are ordinarily composed of 7·5 to 8 per cent. by volume of SO_2, 10 to 11 per cent. of oxygen (of which about 4 per cent. is further utilised to transform the SO_2 into SO_3, and the other 6 to 7 per cent. is in excess), and 80 to 81 per cent. of nitrogen. The furnace gases are hot and cause a draught in the direction of the lead chambers, in which, in spite of the condensation of the sulphuric acid, there is always a slight pressure which is increased by the steam-jets. If the chambers are not perfectly gas-tight losses easily occur, as jets of gas escape at the damaged points.

(*c*) **Rotary Mechanical Furnaces for Burning Pyrites.** These are more expensive than Maletra furnaces and require motive power, and also produce much dust, so that they require large and perfect dust chambers; when contact sulphuric acid is to be made the gases must be filtered through quartz sand moistened with sulphuric acid. These furnaces have, however, the advantage that they can be fed much more regularly without the entry of a large excess of air; also they greatly economise manual labour, which is of special advantage where this is very dear.

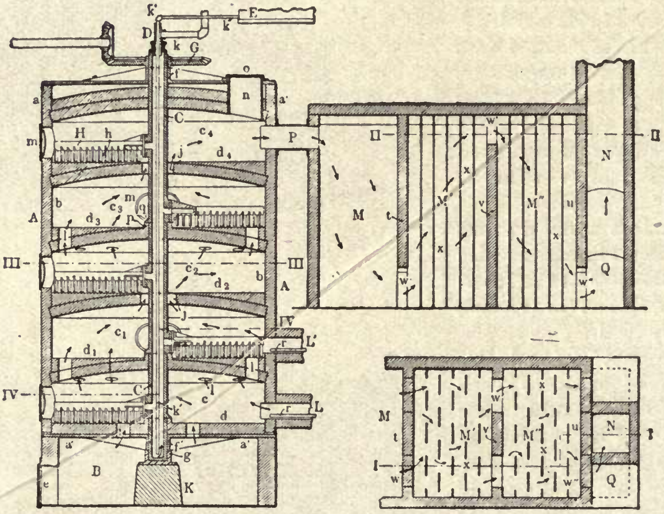


FIG. 102.

These furnaces were introduced industrially after the year 1870 by the brothers Macdougall of Liverpool, but presented so many inconveniences that they have since been repeatedly modified and have been abandoned by some works. Since 1891, however, the improvements introduced have been so marked that they have gradually replaced, with advantage, the Maletra furnaces.

A mechanical furnace which has yielded good results is that used by Frasch since 1890, especially for the treatment of the metallic sulphides obtained in the purification of petroleum. (Sulphur is separated from petroleum during distillation in presence of a mixture of much copper oxide, lead oxide, and iron oxide: *see* Vol. II., "Organic Chemistry"). Fig. 102 shows such a furnace of 5 metres diameter, constructed of refractory fireclay with an outer casing of sheet iron and formed of several vaulted planes on which toothed arms of cast-iron fixed to a central vertical shaft rotate. A continuous current of cold water passes in at the bottom of this shaft through the internal tube $K'D$ from the reservoir placed above the furnace. This water also circulates in the lateral arms in such a manner that all parts of the iron are cooled, whilst in other mechanical furnaces they are always worn out. The hot water which escapes at the top of the tube *k* is utilised in the boilers. The sulphide is added in lumps (passed through a sieve of 15 to 20 mm. mesh) through the aperture, *n*, and on the highest hearth it is moved by the arm, *H*, which carries teeth at a certain angle, from the circumference towards the centre, where it passes through an aperture which carries it to the second hearth, in which the revolving arm carries teeth inclined in the opposite direction, so that the ore is carried from the centre to a suitable opening at the circumference, where it falls on to the third hearth, and so on to the following hearths. An adjustable current of air enters through the lower apertures, *i* and *r*, and causes the combustion of the sulphides, while the exhausted pyrites passes away with not more than 1 per cent. of *S*.

The SO_2 gas and air pass out at the top of the tube *P*, and deposit all the dust in chambers, *M*, *M′*, and *M″*, where they are forced to pursue a lengthy zigzag path before arriving at the tube *Q*, which conducts them to the Glover tower. The burnt pyrites is completely discharged through the apertures *i*. The working of these furnaces appears to be satisfactory, and about thirty were at work in the year 1902.

In 1896 Herreshoff simplified this furnace by circulating air (instead of water), this passing through the central shaft, which is made hollow. The air enters by orifices in the lower part of the shaft outside the burner and escapes through apertures at the top of the shaft. Further, the top of the furnace is used to dry the pyrites, which is distributed regularly on it by means of a vaned arm fixed to the central shaft. Every 60 minutes 125 to 150 kilos of pyrites are loaded at the edge and are carried automatically to the centre, where they fall, through a circular slit 20 to 25 mm. wide round the shaft, uniformly on to the uppermost inner hearth. The shaft is rotated about once in two minutes by spur wheels below. These burners, which are about 2·5 metres high and 4 metres in diameter, have come rapidly into use in Europe and America, owing especially to the great saving in labour, two workmen who receive the weighed pyrites charges on a tip-barrow being able to control some dozens of the burners.

Kaufmann (1901–1906) has modified these mechanical furnaces still further and has increased their capacity from 2 to 5 tons per twenty-four hours. The air circulation has been suppressed, the temperatures on the different hearths being regulated by the feed of the pyrites. In 1901 thirty works in America, Germany, and England introduced many of these furnaces, some of which burn 5 tons of pyrites in twenty-four hours. In order to work seventy of these automatic burners in one works, only two operatives are required. Many of these furnaces have been introduced into Italy, and in Europe about 300 were at work in 1906, the number now being reckoned by the thousand.[1]

INCLINED, CYLINDRICAL, ROTARY FURNACES, into which pyrites continually enters at one end and air for the combustion at the other, were suggested by Ducco in 1906, and after various modifications and experiments made in the works of Rifredi, near Florence; they were also employed in certain other Italian works, but were given up later. The internal surface of these Ducco burners is formed with spiral grooves which facilitate the descent of the pyrites without the production of much dust: there is an ingenious device for feeding in the pyrites continuously.

BLENDE BURNERS. Since a suitable burner was made, the use of zinc blende (ZnS) for making sulphuric acid has extended in all countries. The roasting of blende requires a higher temperature than that of pyrites, complete combustion according to the equation, $ZnS + 3O = ZnO + SO_2$, occurring only at 900 to 1000°; a little sulphate is also formed, but this decomposes at about 1000°, thus: $ZnSO_4 = ZnO + SO_2 + O$. Since, however, blende contains comparatively little sulphur (theoretically 33 per cent. but actually only an average of about 20 per cent.), the burner itself requires heating and must hence be different from pyrites burners.

Attempts were formerly made to burn blende in a flame furnace, but the resulting gases, rich in CO_2 and poor in SO_2 (about 1 per cent.), were unsuitable for the lead chambers. Since 1880 use has been made of muffle furnaces in which the gases from the burning

---

[1] In 1911 1812 Herreshoff burners were at work, 512 in the United States, 357 in Germany, 237 in Italy, 193 in Scandinavia, 147 in France, 116 in Austria-Hungary, 102 in England, etc. Kaufmann burners total 600 (the new type with a single hearth burns 6 tons of pyrites per twenty-four hours). Still more powerful burners are those of Scherfenberg, with seven hearths, burning 8 tons of pyrites in twenty-four hours, and Wedge burners, with a still greater capacity. Herreshoff burners at first cost more than £400 each, but later were made for less that £240.

coal were kept separate; the gases obtained from the blende thus contain 5 to 6 per cent. of SO_2 and can be employed either in lead chambers or for making catalytic sulphuric acid. Blende burners are like Maletra furnaces, or one of the hearths may consist of double bars in which the hot gases from the coal hearth circulate. Special mechanical furnaces have been successfully employed for blende during the last few years.

SULPHUR BURNERS. By starting from crude sulphur in the manufacture of sulphuric acid a greater expense is incurred than when pyrites is used. However, in some cases certain advantages are obtained which cannot be obtained with pyrites. It is of advantage that the gases arriving in the lead chamber should contain a high percentage of SO_2, that is, that they should be diluted as little as possible with inert gases, and this object is attained by burning sulphur, whilst when pyrites is burnt the gases are mixed with air and with much nitrogen derived from the air which has been deprived of oxygen by oxidisation of the iron in the pyrites; they are thus more dilute. In order to obtain an equal production of sulphuric acid lead chambers about 25 per cent. larger are required, while the burners are also more costly. Sulphur also yields a purer acid, free from iron and arsenic.

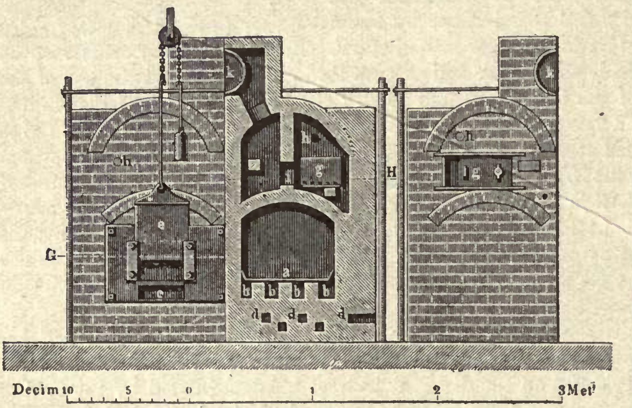


FIG. 103.

The combustion of sulphur is difficult to regulate, because when once it has been started so much heat is developed that the sulphur distils and then enters the lead chamber, yielding a turbid sulphuric acid.

The best of these furnaces is the double one described by Lunge and shown in Fig 103. The sulphur is charged on to iron trays with up-turned rims, *a*, supported in the interior of the brickwork furnace by supports which form the flues, *b*, through which cold air enters from the openings, *d*. This air cools the trays, thus regulating the heat supplied by the burning sulphur, and escapes hot through the aperture *c*, after which it is utilised as a source of heat. The hot fumes from the burning sulphur pass through the aperture *h* into the chamber *g*, where they heat vessels containing sodium nitrate and sulphuric acid for the production of nitrous vapours. Any distilled sulphur is here burnt, and the whole of the gases pass through the tube *i* into the leaden tube *k*, leading to the lead chamber, which is common to two adjoining furnaces. Air may be admitted through the aperture *h* in order to ensure the complete oxidation of the sulphur vapours. In these furnaces 150 kilos of sulphur are burned in twenty-four hours per square metre of tray. For every two furnaces, which are charged alternately, there is one pipe, *k*, which carries the gaseous mixture into the first lead chamber.[1]

LEAD CHAMBERS. The gases pass to the lead chamber by means of a leaden tube (60 to 80 cm. in diameter) at a temperature of 60° to 90°; in some works the temperature of the gas may even be 100°, a temperature which is easily reached in furnaces burning sulphur, whilst gases from pyrites furnaces at 300° to 400° cool down during their passage through

---

[1] As we have already stated, Oddo has proposed (1907 and 1910) to burn sulphur ores directly in somewhat modified mechanical Herreshoff furnaces. He proposed to form briquettes of 5 parts of "sterro" (which contains 40 per cent. of sulphur on an average) with 1 part of crude sulphur, rendered compact in presses heated in furnaces to 140°. The resulting material containing 50 per cent. of sulphur would thus cost about £1 4*s*. per ton at the port of Genoa. It cannot be denied that pyrites of the same strength costs only £1, and has in the past cost less than 16*s*. The other small advantages accruing to sulphuric acid manufacturers using this conglomerate of Oddo do not appear sufficient to induce them to abandon the use of pyrites. This would only be possible if the sulphur-containing agglomerates were placed on the market at a price lower than or equal to that of pyrites. If its use were to become very general, it would be possible to place it on the market at lower prices.

the Glover tower. The lead chambers are supported on pillars at a height of from 2 to 3 metres above the ground, so that the ascending current of hot gases from the furnaces may be utilised, and in order that any leakage of the condensed acid through the chamber floor may always be noticed (Fig. 104). At the bottom a firm wooden framework carries the base of the chamber which consists of closely-fitting wooden planking 3 cm. thick, bolted together with bolts well sunk and covered with putty; the floor of the chamber rests on this platform and is formed of welded leaden plates of a thickness of about 3 mm. This leaden floor has turned-up sides, 50 cm. or more high, and holds the acid which is formed. The walls and roof are supported by a firm wooden framework and are fixed to this by strips of lead to which they are soldered. The vertical walls do not touch the bottom, but hang at a distance of 1 to 2 cm. above it, so that the bottom of the chamber is closed by a kind of hydraulic seal formed of the condensed acid.

The volume of the lead chambers must be large, because the yield is better when the reacting gases are well mixed, and since 8140 litres of reacting gases are formed per kilo of sulphur in the pyrites, the volume is so reckoned that 1½ kilos of pyrites burnt in twenty-four hours correspond with about 1 cu. metre in the lead chamber.[1]

A system of three or four chambers is generally used. The first is the largest and collects the greater portion of the acid; the last (the tail chamber) is the smallest, and is used mainly for cooling and drying the gas. The draught in the chambers is produced by the hot gases which enter from the Glover tower, by the condensation which occurs in the chambers, and by the absorption of gas in the Gay-Lussac tower.

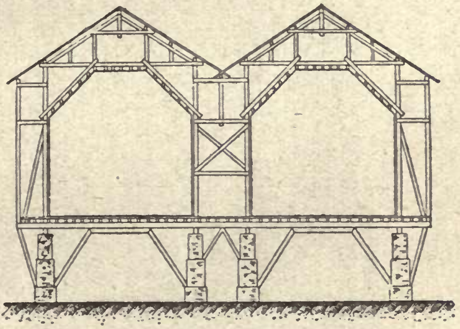


FIG. 104.

Sufficient steam must be passed into the lead chambers to transform all the SO_2 of the burning sulphur into sulphuric acid, and to yield an acid in the first chamber of 50° to 52° Bé., that is, about 2 kilos of steam per kilo of sulphur. When Glover towers are used 60 per cent. of such amount of steam is sufficient. Nowadays the steam is almost universally replaced by pulverised water, as was suggested by Sprengel in 1873.[2]

The *nitrous fumes* are produced in the *nitre pots*, which are placed between the dust flues and the Glover tower and are heated by the gases from the pyrites burners. The reagents consist of equal weights of nitre and of H_2SO_4 at 50° Bé. They are contained in small lead vessels, and a residue of sodium bisulphate is obtained.

---

[1] These chambers last for fifteen to twenty years, according to the intensity with which they are worked. Good results are obtained with chamber systems of 4000 cu. metres, in connection with which about 7 tons of pyrites are burned in twenty-four hours. Each cubic metre of volume of such a chamber requires about 200 to 250 kilos of lead plates of 3 mm. thickness.

[2] The intensification of the working of lead chambers, with a view to diminishing the cost of the acid and rendering it easier to cope with the competition of contact acid, has resulted in a yield of 10 kilos or more of acid of 52° Bé. per twenty-four hours per cu. metre of chamber space, instead of 3 to 4 kilos with slow, or 5 to 6 with medium working. With this intensive working, however, the temperature of the first lead chamber becomes excessively high (140 to 150°) and the lead is consequently damaged. This trouble is completely avoided and at the same time a marked saving effected if the steam is replaced, in the first and second chambers, by atomised water (by suitable injectors placed at the top of the chamber along the longitudinal median and fed by a small pump at 5 atmos.). In this way the temperature falls to about 100°, while with moderately rapid working, 85° to 90° is obtained in place of 110° to 120° (with steam). Pulverised water cannot, however, be used if the working is only moderately rapid, since even with steam the temperature in the first chamber is only about 65° in winter and 80° in summer, and if pulverised water is employed, the temperature would be lowered by about 15° and the chemical reactions in the chamber would be greatly retarded.

For a works with 5000 cu. metres of lead chamber, the production of sulphuric acid with slow working is about 20 tons per twenty-four hours, the coal consumed being 360 tons per annum. For the sample plant worked intensively with steam, an output of 40 tons of acid per twenty-four hours is obtained, 720 tons of coal being burnt per annum. If the steam is replaced by pulverised water, the cost of the coal is saved, the water requiring only a small pump consuming about 1 h.p. With intensive working, 25 per cent. of the nitrate is also saved, the total saving effected by the use of pulverised water being about 1*s*. 7*d*. per ton of acid at 52° Bé.

In some cases, instead of employing nitre pots, nitric acid is dropped directly with the nitrous sulphuric acid into the Glover tower. In Fig. 105 an old plant is shown which would have to be modified in various respects to-day.

The gases from the burners, *A*, pass into the dust flues, and then through the pipe, *G*, into the Glover tower, *E*, and thence at the top into the first lead chamber, *C*. They pass out from the opposite end of this chamber below and ascend by a tube into the upper part of a second chamber, and so on through a third chamber or more. They then pass into the vessel, *M*, from which they enter the Gay-Lussac tower, *D*, from the top of which a spray of sulphuric acid falls from *N* and dissolves the nitrous fumes. This acid proceeds through the tube *L* to the pulsometer, *H*, which raises it through the tube *K* to the top of the Glover tower, where the nitrous vapours are regenerated.

In ordinary lead chambers, working regularly, 2½ to 3½ kilos of H_2SO_4 calculated at 100 per cent. can be produced per cubic metre in twenty-four hours, this corresponding with 4 to 5½ kilos of sulphuric acid of 50° Bé.

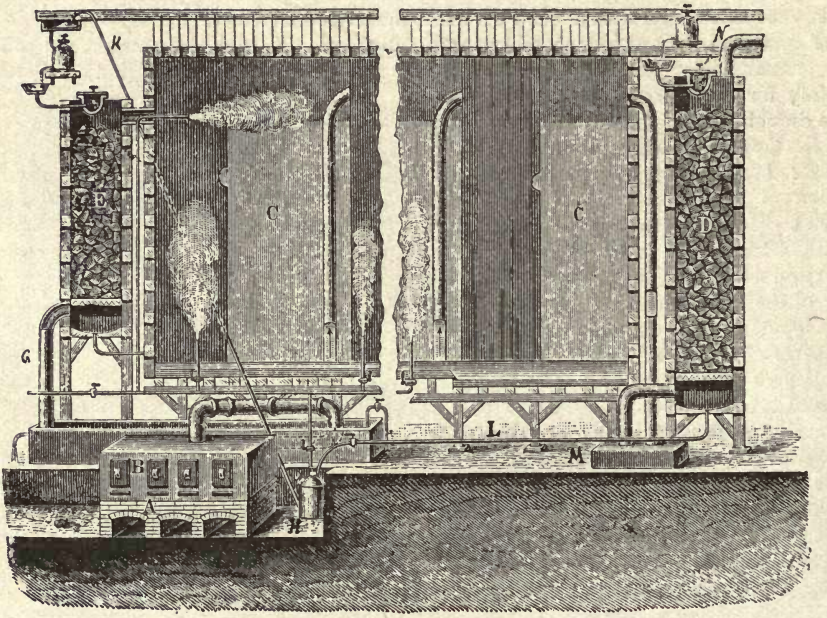


Fig. 105.

TANGENTIAL LEAD CHAMBERS. In 1882 Abraham stated that the gases entering the ordinary lead chamber pursue a spiral path. In 1898 Th. Meyer (Ger. Pat. 301,376) observed that if gases are made to enter tangentially at the base of a cylinder and to issue from the top through an aperture in the centre of the cover, the gas pursues in the interior of the cylinder a spiral course, and the same thing occurs if the gas enters tangentially at the top and issues at the base through a central aperture as indicated in Fig. 106*a*. In ordinary lead chambers the gases have a tendency to pursue a rectilinear path and do not mix much, so that it is necessary to construct very large chambers, which are very costly. If, on the other hand, the chambers are constructed of a cylindrical shape and the gases enter tangentially at the top and issue through a hole in the centre of the floor (Fig. 106*b*), contact between the gases is so intimate and rapid that the same quantity of sulphuric acid may be produced with two-thirds of the volume of the ordinary lead chamber, and thus with a correspondingly less expense for plant. In the cylindrical lead chambers 172 kilos of 3 mm. sheet lead are used per cubic metre, whilst in the ordinary rectangular chambers at least 200 kilos are required. In 1903 tangential lead chambers of a combined capacity of 40,000 cu. metres had already been constructed in various works and produced 160 tons of H_2SO_4 per day. Each cubic metre of the chamber produces 4 kilos of H_2SO_4, and in some cases even 6 kilos, in twenty-four hours.

Fig. 106 shows diagrammatically a system of five tangential chambers in a sulphuric acid factory. The shaded square on the left indicates the pyrites burners and above this is the Glover tower and below the Gay-Lussac tower, the latter receiving the gas which has passed through the five chambers. The temperature in the first chamber is regulated by means of a group of lead tubes which pass from the top almost to the bottom of it and contain circulating cold water, used subsequently to feed the boilers. More recently this bundle of tubes has been replaced by a large central ring open above and at the base, through which air circulates, so that the true chamber is formed by the interval between the external cylinder and the internal cylinder constituting the ring. In 1906 Th. Meyer (Ger. Pat. 186,164) improved the system by increasing the size of the first chamber and making the next one or two chambers gradually smaller, introducing the gas tangentially at two points at different heights in each chamber in order to obtain more complete admixture.

In 1910 (Ger. Pat. 226,792), Meyer further improved the process by tangential aspiration of the gas in a dead zone at the bottom of the tower and reintroduction of it tangentially halfway up the chamber. Later chambers were constructed 14 metres high and 11·5 metres wide, these being almost as large as tower chambers (*see later*). In 1913 there were 40 works with tangential chambers in Europe, two of them in Italy.

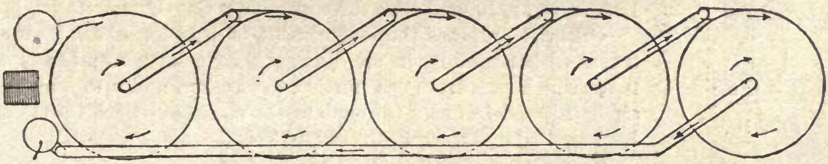


FIG. 106.

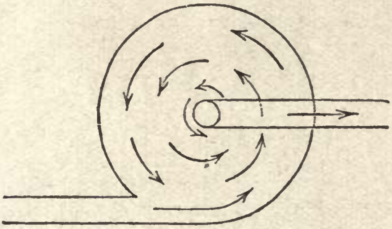


FIG. 106*a*.

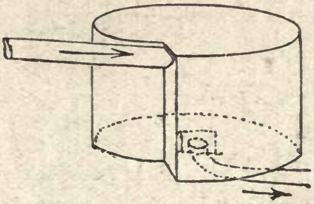


FIG. 106*b*.

An important modification of the form of the lead chamber has also been introduced industrially by F. J. Falding of New York (U.S. Pat. 932,771 of 1909). He uses a single lead chamber, one and a half times as high as it is broad. The gases from the Glover tower enter at the top and pass out at the base, but since they are still very hot they are cooled in a cylindrical tower before being sent into the Gay-Lussac tower. By Falding's system 40 per cent. of lead is saved for a given yield. With a single Glover tower several of these vertical chambers may be fed at once. It should, however, be noted that in 1908 O. Guttmann had already proposed and described lead chambers similar to those patented by Falding (*see* p. 306, Tower Chambers).

PLATE-TOWERS OF LUNGE AND ROHRMANN. For the purpose of securing more intimate contact of the gases and obtaining a more rapid production of acid Lunge in 1887 suggested the replacement of lead chambers by towers formed of close-fitting plates of perforated earthenware. These towers were gradually improved and in 1903 23,000 plates were in use altogether in various works, producing 150 tons of H_2SO_4 per day. 100 cu. metres in these towers produce as much as 750 cu. metres of tangential chambers, or 1100 cu. metres in rectangular chambers.

The prime cost of these towers is somewhat high, and for an equal production of acid towers of 100 cu. metres would cost about £800, whilst 750 cu. metres of tangential lead chambers would cost about £560.

Plate-towers have also been proposed for the diminution of the volume of the lead chambers by interposing them between one chamber and another. They may also replace

Gay-Lussac towers, as we see in Fig. 107. The practical advantages of these towers have been excessively exaggerated by some and much depreciated by others. As towers interposed between the chambers they increase the resistance to the current of gas, and this is remedied by means of a hard-lead aspirator at the tail end of the chamber. The yield from these towers is especially high if they are fed from above with nitrous sulphuric acid. Large economies of space are effected by their use and the supervision is rendered easier. In England these interposed towers are somewhat common, but the replacement of steam by water-sprays has not been found advantageous, perhaps because steam is very cheap in England.

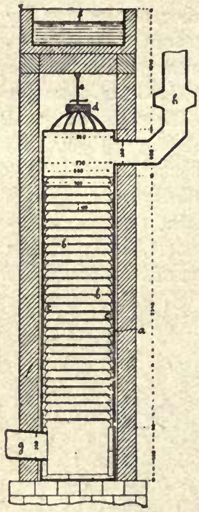


FIG. 107.

In Fig. 108 are shown drawings of a works, both in section and in plan, for the production of eleven tons of H_2SO_4 per day. The lead chamber, *B*, is 7·25 metres high, 8·4 metres wide, and 25 metres long, and receives the furnace gases through two Glover towers, *G* and *A*. The gases then pass through five plate-towers, as is seen on the plan in the figure, and are collected by the aspirator, *Z*, which passes them through a small plate-tower acting as a Gay-Lussac tower, L_1, and then through a large Gay-Lussac tower, L_2.

Gilchrist proposes the replacement of lead chambers by towers traversed horizontally in all directions by a large number of lead tubes which pass from one portion to another, and into which cold air is injected in order to regulate the reaction. Such towers have been applied in America (*see later*, p. 306).

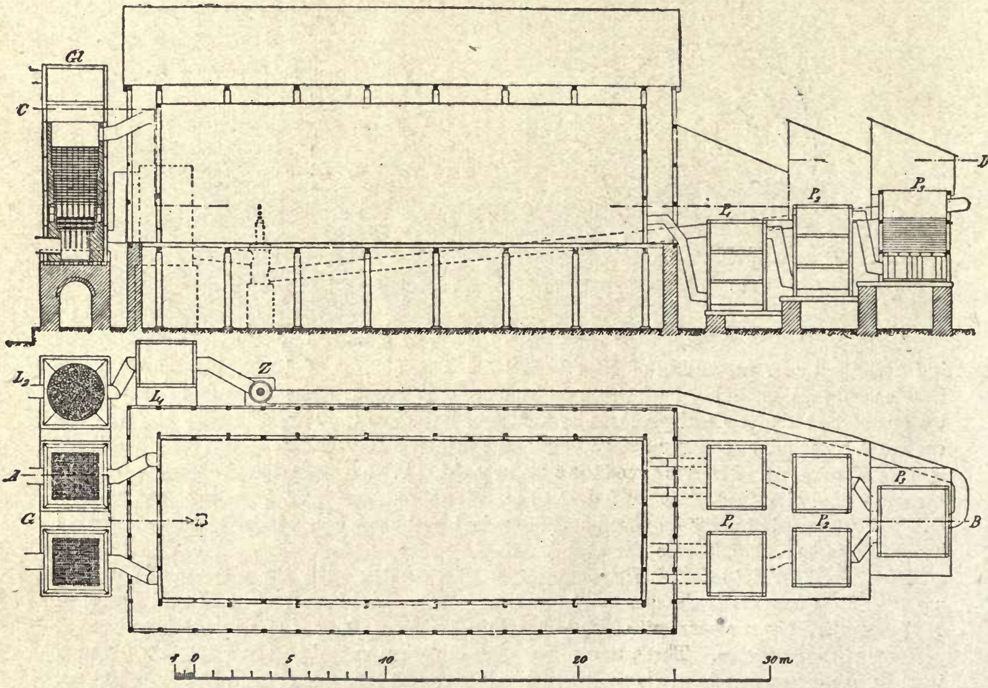
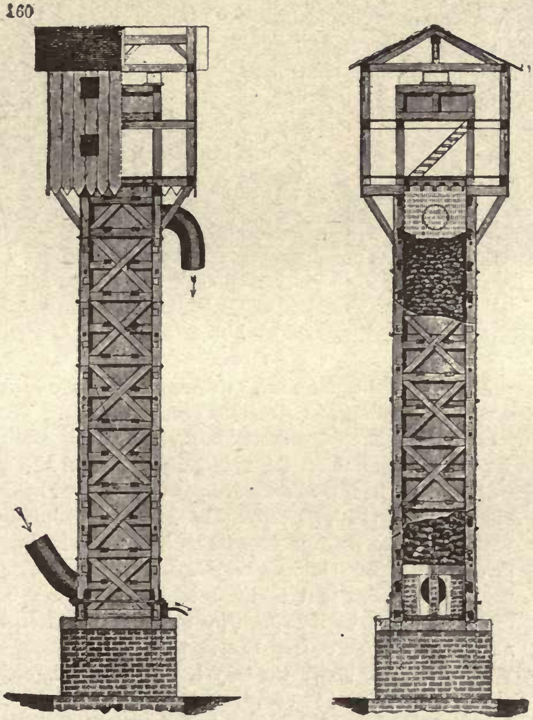


FIG. 108.

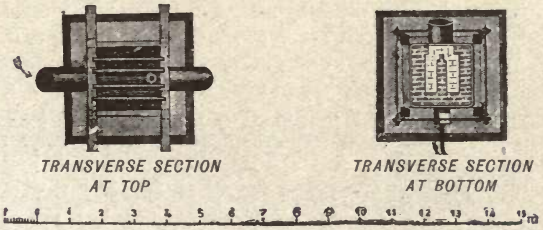
GAY-LUSSAC TOWERS. These towers were suggested by Gay-Lussac in 1827 and were applied for the first time at Chauny in 1835. In Germany they were constructed from stoneware tubes of 80 cm. diameter and 80 cm. high superposed to a height of 12 metres. These towers are to-day built entirely of lead (Fig. 109) and about 2 metres above the ground, in the form of cylinders 12 to 13 metres high and 2½ to 3 metres in diameter, supported by vertical beams, and dipping almost to the bottom of a lead receiver, which is turned up at the sides to a height of about 15 cm., so that a hydraulic seal is formed by the acid which collects. The tower is filled inside with acid-resisting bricks or stones, and at a height of a metre this subdivided material is supported by a strong grating of lead. The gases from 4000 cu. metres of lead chambers can be handled in such a tower of 55 cu. metres capacity.

The towers were at one time filled with lumps of coke, but these caused loss of nitre and other inconveniences (obstructions, etc.).[1] Nowadays they are filled up to one-third from the bottom (where the hotter gases enter) with small cylinders or clay spheres which are close-packed; they are followed above by a layer of hard compact coke. Nitrous gases enter at the bottom from the last lead chamber, and concentrated sulphuric acid of 60° to 62° Bé. (collected from the Glover tower) falls from above, being subdivided into thin continuous streams by means of the apparatus indicated in Fig. 110, which also forms the roof of the tower, being closed by grooves forming a hydraulic seal; the acid spray dissolves



ELEVATION

SECTION



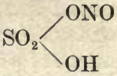
TRANSVERSE SECTION
AT TOP

TRANSVERSE SECTION
AT BOTTOM

Fig. 109.

---

[1] When sulphur is burnt the tower need only be 8 metres high. With pyrites burners the height varies from 12 to 18 metres, according to the size of the chambers. The volume of the Gay-Lussac tower when it is fed with an acid of 61° Bé. should be about $1\frac{1}{2}$ per cent. of the volume of the lead chambers, and if an acid of 60° Bé. is used, its volume should be 2 per cent. of that of the chambers. Towers of medium cross-section have sides about 2 metres long.

the nitrogen oxides contained in the gases issuing from the lead chamber and forms the so-called nitrous sulphuric acid, which is a solution of nitrosylsulphuric acid,  $SO_2\begin{cases}ONO\\OH\end{cases}$ in sulphuric acid.

About 500 litres of sulphuric acid of 62° Bé. are passed through the Gay-Lussac tower for every ton of pyrites burnt, and at the base of the tower a nitrous sulphuric acid of 59° to 60° Bé. collects, containing 7 to 8 per cent. of nitrosylsulphuric acid (= 2·4 per cent. N_2O_3), and is titrated with a solution of potassium permanganate. The absorbing power for nitrous fumes appears to be greatly increased, in fact, more than doubled, if an acid of 54° to 56° Bé. is used for absorption (Heinz and Petersen; Ger. Pat. 217,723 of 1908).

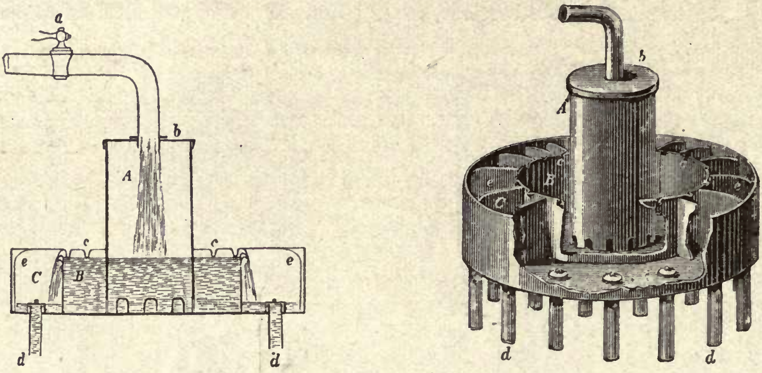


Fig. 110.

H. Petersen (1909) attributes the low absorptive power of Glover acid to the presence of ferrous sulphate, and he therefore proposes to oxidise it to ferric sulphate, either mixing it with a little of the nitrous acid or, better, by feeding the Glover tower acid directly into the first Gay-Lussac tower; the oxidised acid from the latter is then sent to the second Gay-Lussac tower, marked loss of oxides of nitrogen being thus avoided. Plate towers are also used nowadays instead of Gay-Lussac towers.

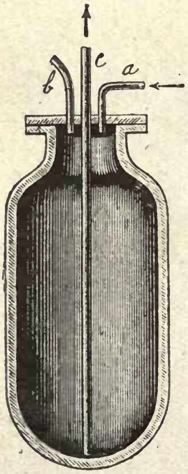


Fig. 111.

The acid for use in the Gay-Lussac towers is collected in receivers of lead, stoneware, or cast-iron (pulsometers, acid elevators, pressure pots, acid eggs, or Montejus), from which it is raised through stoneware or leaden pipes by means of air from a pressure-pump.

These elevators are known in various forms, and to-day those are preferred which work automatically. The simplest non-automatic type is illustrated diagrammatically in Fig. 111, and consists of a vertical cylinder of cast-iron or lead into which the acid enters through the tube *a* communicating with a large reservoir. When the cylinder is full the cock on this tube is closed and that conveying the compressed air is opened; this then acts on the surface of the acid and forces it to rise to the desired height up the tube *c*, which reaches to the bottom of the cylinder. When the cylinder is empty the operations are recommenced as at first by filling the pot again with acid. In order to prevent the acid from getting accidentally into the air-tube and pump, the air-tube reaches the cylinder at a height of 3 or 4 metres from the acid, and there is always a cock attached to the cylinder by which the air pressure may be relieved when operations are to be stopped. An automatic pulsometer or acid elevator is shown in Fig. 112. The acid to be raised is kept in the reservoir, *h*, and descends into the cylinder, *b*, raising the valve, *i*, and entering the elevator through the tube *g*. The air displaced by the acid passes through the small U-tube *f* and escapes through the tube *d*. If the cock of the tube *e* is opened, then before the pulsometer is full the compressed air which passes in through the tube *e* escapes through the tubes *f* and *d*, but when the acid reaches a level higher than *m* the tube *f* is filled and the air compression closes the valve, *i*, and prevents any further arrival of acid, whilst that contained in *b* rises up the tube *d* to the height required as long as the pressure lasts. When the vessel, *b*, is empty or almost empty, the compressed air is again able to escape through *f* and *d*, and the pressure which had shut off the valve, *i*, ceases, so that acid enters and the operations proceed afresh. The cylinder, *b*, can be filled and emptied about thirty to forty times an hour. The Schütze acid elevator is very useful for economising compressed air (and therefore motive power) and works still more automatically than the others. While the liquid to be elevated enters through the valve *A* (Fig. 113), the air at first contained in the receiver escapes through the valve *D*. When the liquid reaches the upper ball, B_1, of the float, *C*, this rises and its upper arm closes the outlet valve, *D*, at the same time opening the valve *E*, which gives access to compressed air, and the liquid then rises through the tube *G* to the desired height. When the level of the acid in the receiver has dropped to the lower bulb, *B*, of the float, this drops and closes the valve *E*, and the remaining air pressure suffices to empty the receiver completely. Only then does the escapement valve, *D*, re-open, so that all pressure ceases, and the receiver is again filled quite automatically by the acid which enters from *A* by lifting the ball-valve, *A*, which was closed while there was air pressure in the receiver. During the filling of the receiver the upper part of the tube *G* remains full, because the ball of the valve *G* drops.

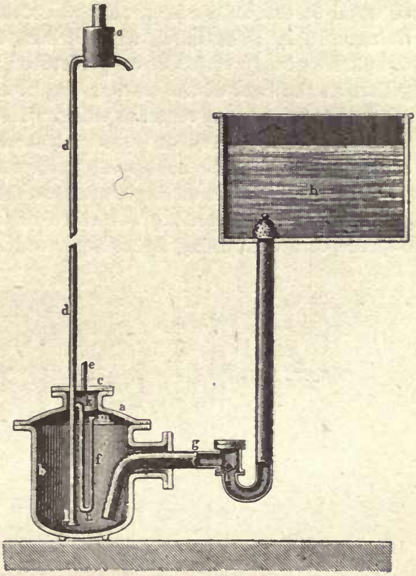


FIG. 112.

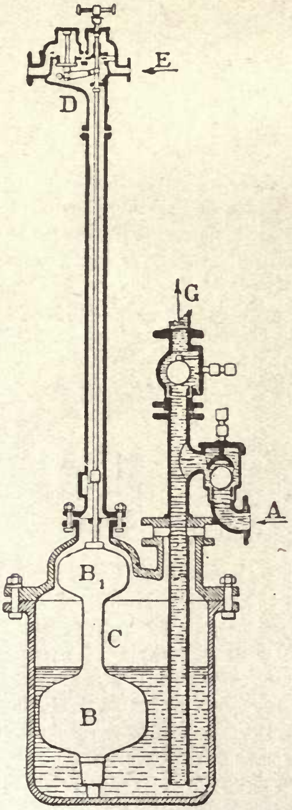


FIG. 113.

Forty-five pulsations (fillings of the receiver) may be obtained per hour. In order to raise a liquid of density 1·8 to a height of 10 metres the air must have a pressure of about 2½ atmospheres. This apparatus may be used for any liquid, and for acids it is constructed of cast-iron which may be lined with lead, or in the case of hydrochloric acid it is made of stoneware, and in the case of fatty acids, of copper.

We may here describe another apparatus for raising liquids which is often used industrially, and which we have already mentioned in the chapter on the extraction of sulphur from the interior of the earth by the Frasch system (p. 217). This is the so-called *Mammoth pump*. With an equal air pressure a heavy liquid may be raised to a greater height than with an ordinary pump, if the column of liquid to be raised is rendered lighter by emulsifying it with air or sometimes even with water. If the sulphuric acid in the tank *E* (Fig. 114) is to be lifted into the receiver, *L*, it is first passed into a U-shaped tube, *G*, at a lower level than the tank *E*; at the lower part of this U-tube there enters on the left a tube, *A*, from which a very fine jet of compressed air is blown, which emulsifies the liquid and raises it to the tank *L* by the long tube, *BK*. At the top the air separates from the liquid and is set free.

The Glover tower serves three important purposes: firstly, it cools the furnace gases down to 60° to 100°; secondly, it concentrates the chamber acid of 50° to 53° Bé. up to 60° to 62° Bé.; thirdly, it denitrifies the acid proceeding from the Glover tower, and at the same time washes the furnace gases. It consists of a cylindrical leaden tower about 3 metres in diameter and 8 to 10 metres high (Fig. 115), supported by an external framework of wood or cast-iron and protected inside to two-thirds of its height by an acid-resistant lining. It is then filled with bricks of the same material or with small cylinders or spheres of clay which lie on perforated horizontal earthenware plates supported by small pillars at the base of the tower; the base is united to the cylindrical portion and rests on stones contained in a vessel in which water circulates in order to cool the base of the tower. The latter is raised two or three metres above the ground so as to allow room for the spiral coolers which cool the acid issuing still very hot (up to 150°) from the base.

In the upper part of the tower there are two lead vessels, one of which contains nitrous sulphuric acid, comprising two-thirds of the whole acid used, and of a strength of 56° to 60° Bé., and containing 2½ to 3 per cent. of N_2O_3, and the other sulphuric acid from the chambers. The two supplies of acid are slowly distributed as a spray by arrangements similar to those shown in Fig. 110. They mix in the tower and descend against the current of hot SO_2 gases coming from the pyrites burners through an earthenware pipe encased in metallic sheeting. The nitrous vapours are liberated and escape into the top of the tower together with SO_2 and air, passing out through a leaden tube which conducts them to the upper part of the first lead chamber. At the base of the tower concentrated sulphuric acid, up to 63° Bé., collects and is free from nitrous compounds.[1]

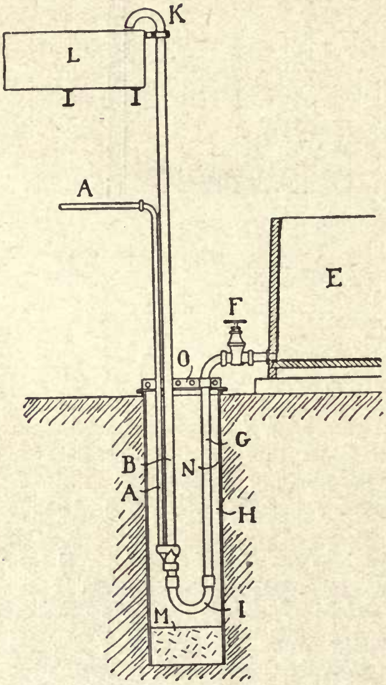


FIG. 114.

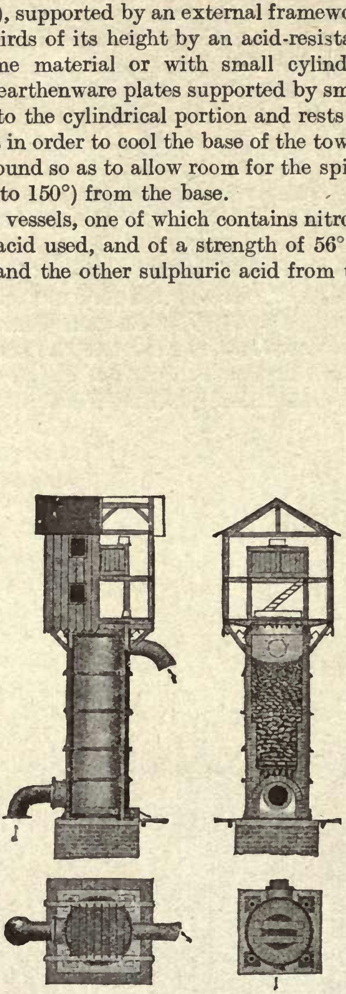


FIG. 115.

---

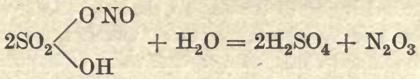
[1] For a system of lead chambers of 4000 cu. metres capacity, a Glover tower of about 70 cu. metres is required, or less, unless all the chamber acid is concentrated to 62° Bé.; ordinarily the capacity of the Glover tower is 2 per cent. of that of the lead chambers. 4000 kilos of Spanish pyrites burnt in twenty-four hours yield 2040 kilos of acid of 53° Bé., and if this is all passed into the Glover tower 1670 kilos of 62° Bé. are obtained. Usually, however, part of the acid is consumed at a strength of 53° Bé. The work of the Glover tower is not remunerative if the gas from the furnaces has a temperature below 250° (sulphur burners). For each 100 kilos of sulphur burned, or the corresponding quantity of pyrites, the Glover tower receives 800 to 1500 kilos of acid (two-thirds of which is nitrous), according to the temperature of the gas which escapes from the burners, less being required when it is hotter.

It is not advisable to concentrate the acid in the Glover tower to a strength above 63° Bé. because otherwise the leaden walls of the tower are attacked. Ordinarily acid of 60° to 61° is obtained and passes out of the tower at a temperature of 125° to 145°, after which it is cooled with water which passes through lead coils, before being collected in tanks of cast- or wrought-iron. About 40 per cent. of the water vapour required in the lead chambers is furnished by the Glover tower. In order to produce 150 kilos of sulphuric acid of 53° Bé. without the Glover tower, 22 kilos of coal are necessary for steam production, whilst when the Glover tower is used only 13 kilos are required for this purpose.[1]

Hegeler and Heintz (Fr. Pat. 341,257 of 1904) appear to have succeeded in obtaining sulphuric acid of 66° Bé. directly in the Glover tower by regulating the temperature by suitable means, so that the leaden walls of the chamber are not attacked, and by forcing the nitrous gases back to the base of the tower by means of a fan in order to produce more SO_3 and thus more sulphuric acid.

The reactions which occur in the tower are, according to M. Neumann (1906), the following: In the lower part of the tower, where the temperature is higher, there is a reducing action (I), and in the upper part where the temperature is lower an oxidising action (II):

(I) (α)

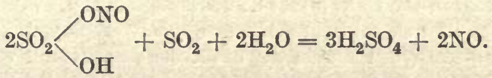


$$2SO_2\left\langle\begin{array}{l}O\cdot NO\\ OH\end{array}\right. + H_2O = 2H_2SO_4 + N_2O_3$$

(β) $$N_2O_3 + SO_2 + H_2O = H_2SO_4 + 2NO$$

or altogether:

(α + β)

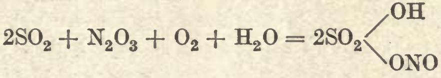


$$2SO_2\left\langle\begin{array}{l}ONO\\ OH\end{array}\right. + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

Whilst the reaction (α) causes evolution of heat, the action (β), in accordance with which the N_2O_3 is reduced to NO, absorbs heat, and, therefore, in order to facilitate the formation of sulphuric acid (3 mols.) in the Glover tower it is necessary to maintain the lower portion of the tower at a high temperature (150° to 160°), which is also essential in order to decompose the nitrous sulphuric acid. In the upper part of the tower where the gases rise together with NO, the following reactions occur:

(II) (γ) $$2NO + O = N_2O_3$$

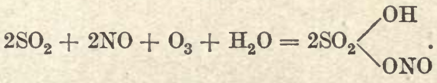
(δ)



$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\left\langle\begin{array}{l}OH\\ ONO\end{array}\right.$$

or altogether:

(γ + δ)



$$2SO_2 + 2NO + O_3 + H_2O = 2SO_2\left\langle\begin{array}{l}OH\\ ONO\end{array}\right. .$$

These two reactions are exothermic and are facilitated by gradual abstraction of the heat evolved, so that some nitrosylsulphuric acid may be produced in addition to that already formed and yield sulphuric acid in the lower part of the tower.

Neumann himself (Ger. Pat. 169,729) proposed the production of the greater part of the sulphuric acid by means of a series of three or four communicating Glover towers cooled above and heated below by means of the hot gases from the pyrites burners during their passage to the first tower; in the last tower, where the gases are poor in SO_2 and O, a higher temperature (200°) is maintained, this also facilitating the reaction.

The firm of Niedenführ construct Glover towers in which the gases are cooled half-way up the tower and escape without cooling the nitrous sulphuric acid which descends (Ger. Pat.

---

[1] *Steam Boilers.* For the production of steam for the chambers and acid pumps, two small boilers are employed by preference, because while one is working the other can be cleaned, and the manufacture thus continues without interruption. It is calculated that for 1000 cu. metres of chamber volume the consumption of coal for the boilers should be on the average 350 kilos per twenty-four hours.

206,877); the substitution of all the lead chambers by a number of Glover towers has even been proposed (Ger. Pat. 217,036).[1]

A small portion of the nitrous products is lost, and in order to reduce this loss to a minimum two parts of nitrous sulphuric acid to one part of lead-chamber acid are passed through the Glover tower. When the temperature in the lower part of the Glover tower is excessively high, the reduction of the nitrogen oxides may lead to the formation of elementary nitrogen, thus causing losses and, therefore, a larger consumption of nitrate.

REGULATION OF THE PROCESSES IN THE LEAD CHAMBERS. If 1·9 kilos of Spanish pyrites are to be burnt per cubic metre of chamber space per twenty-four hours, it is necessary to regulate the draught so that the furnace gases contain about 7·5 per cent. by volume of SO_2, and the final gases which escape from the chamber, from 6½ to 7½ per cent. by volume of oxygen.[2]

The entry of the steam or pulverised water is regulated in such a way that the acid formed in the chamber is maintained at a definite concentration of 50° to 53° Bé., but that in the last chamber, into which no steam is injected, and in which the gases are poor and partially exhausted, is sometimes only at 40° Bé. The acid which falls from the roof and the walls varies rather rapidly in concentration with the variation in the amount of steam, and is ordinarily more concentrated by 2° to 3° Bé., so that an excess or deficiency of steam may be detected by frequent titration of this acid, which is collected through suitable apertures and channels constructed along the internal walls of the chamber.

The temperature inside the lead chamber rises or falls with increase or diminution of nitrate, and if the temperature of the vapours which enter the chamber is 70° to 90°, then the most suitable mean temperature in the first chamber is about 65°, whilst in the second chamber it is 55°, and in the third about 35°, although in some works to-day temperatures of about 100° in the first chamber are advantageously employed. The lead is then more rapidly attacked, especially if the quantity of nitrous fumes is not very carefully regulated. The gases are led from the last chamber through a long leaden tube to the base of the Gay-Lussac tower, which is placed close to the Glover tower. The colour of the vapours in the first chamber should be very pale and should gradually change as one gets further from the point of entry, through the whole chamber system, acquiring a more and more intense yellowish-brown colour, and at the entrance to the Gay-Lussac tower should be markedly reddish-brown. The gases which escape from this tower should be colourless.

The acid which collects at the base of the chamber is removed from time to time, but to an extent of not more than 10 cm. each time, a layer of at least 20 to 30 cm. being always left.

The most important control of the progress of the reactions in the lead chambers is effected by watching the work of the towers, which for convenience should be placed close together (*see* Fig. 108, p. 300), and by analysing the escaping gases by the usual analytical methods. The SO_2 of the furnace gases is titrated with a solution of $\frac{N}{10}$ iodine by Reich's method.

---

[1] *Tower chambers.* Since 1910 sulphuric acid works have been constructed in which the chambers are replaced by large towers, as suggested by Opl. In these as much as 37 kilos of acid at 53° Bé. are produced in twenty-four hours per cu. metre of tower-space, the consumption of nitric acid of 36° Bé. being 0·35 per cent. By this means only one-third of the space and only two-thirds of the lead are required, although considerably more power is required to circulate the gases to such great heights and against such great resistance. G. Duron (Ger. Pat. 267,138 of 1912) has improved this tower system, but if there is not a very efficient dust chamber to purify the gas, a very impure acid is obtained, although its concentration easily reaches 60° Bé.

O. Wentzki (Ger. Pat. 230,534, 1910) suggests the use of lead chambers in the form of horizontal, revolving drums, which would produce several dozens of times as much acid per cu. metre as the ordinary chambers (!).

[2] In order to start work in lead chambers the pan is filled with sulphuric acid of 45° to 50° Bé., so that a hydraulic seal is obtained with the vertical walls. SO_2 and nitrous fumes are then introduced until the gases in the last chamber have a yellowish-brown colour. For this purpose 12 to 15 per cent. of nitrate is required compared with the weight of sulphur which is burned, and if very intense working takes place as much as 20 per cent. may be necessary. On the second day air and steam are also introduced, and on the third day regular work may be started in all the chambers. In the first chamber there should always be a slight excess of pressure, while from the second and third this should almost disappear, or there may even be a slight vacuum in the third. Gases from sulphur burners should contain about 11 per cent. of SO_2 and those from pyrites burners about 7·5 per cent.

An analysis of the gas proceeding from the Glover tower gave the following results :

SO_2	O	NO	N_2O_3	N_2O_4	N
6·9%	10·9%	0.113%	0·036%	—	92·05%

At the outlet of the last (fourth chamber), the composition was :

—	7·3 %	—	0·182 %	0·121 %	92·57 %

75 per cent. of the sulphur dioxide contained in the gases escaping from the Glover tower is transformed into sulphuric acid in the first chamber, 20 per cent. in the second, and 4½ per cent. in the third. The exhausted gases which escape from the Glover tower are observed by means of a window placed in the pipe which conducts them to a suitable chimney in which the draught through the whole of the lead chambers may be suitably regulated by means of automatic valves, an aspirator being used when required. Naturally the gases which issue from the chimney must not contain SO_2 or nitrous vapours.

SULPHURIC ACID FROM GYPSUM ($CaSO_4$). For some years attempts have been made to utilise the sulphur present in gypsum—which occurs very abundantly in nature and is very cheap—for the manufacture of sulphuric acid. Since 1905 patents have been filed for various processes in which the sulphuric acid or sulphur dioxide of the sulphate is liberated at a very high temperature in presence of silica, carbon, etc.[1] It appears that Germany made wide use of these processes during the European War, as the importation of pyrites was prevented.

CONCENTRATION OF H_2SO_4. The sulphuric acid from the chambers of 50° to 52° Bé. (65 per cent. H_2SO_4) is not concentrated in the Glover tower, as otherwise it would become dirty, but is evaporated in leaden pans up to a strength of 60° Bé. (78 per cent. H_2SO_4). Any further concentration is conducted in vessels of cast-iron and not of lead, because at the temperatures required the lead becomes soft and is then attacked. The rims of these vessels are made of lead so that they may resist the action of the acid vapours which are evolved. So-called English sulphuric acid of 64 Bé. (86 per cent. H_2SO_4) is thus obtained. With three leaden pans 2 metres long, 1 metre wide, and 30 cm. deep, 3 tons of sulphuric acid of 52° to 53° Bé. may be concentrated up to 60° in twenty-four hours, with a consumption of half a ton of coal. They are heated by means of the hot gases from the burners, which traverse the surface of the acid, or if a purer acid is required, the heating may take place below the pans, which in this case rest on iron plates. In some localities the concentration is effected by means of high-pressure steam circulating in leaden coils immersed in the acid.

In some smaller works, especially in England, acid of 66° Bé. (which is really 65·7° Bé

---

[1] *Sulphuric acid from gypsum.* H. Hilbert (Ger. Pat. 207,761, 1908) heats a mixture of gypsum, silica, and alkali sulphate in an electric furnace; evolution of SO_3 begins at 1250° and is complete at 1400°. The residue consists of glass (calcium and sodium silicates).

In 1909 H. Trey prepared $SO_2 + O + H_2O$ by heating gypsum (with less than 0·5 per cent. of Fe_2O_3 as catalyst) to redness in presence of silica; the gases were then dried and passed over the ordinary catalytic material, SO_3 resulting. The residue serves for glass-making. This process appears to have been successfully applied in 1910 (Ger. Pat. 207,761).

M. Prud'homme (Fr. Pat. 400,030, 1908) heats calcium or other sulphates in an electric furnace with or without silica or alumina or oxides of iron, and obtains sulphur trioxide or $SO_2 + O$.

R. Wedekind and Co. (Ger. Pat. 232,784, 1910) assert that attempts to obtain SO_3 from gypsum and sand in retorts or muffle furnaces do not succeed. They obtain good results, however, by mixing 5 parts of gypsum ($CaSO_4 + 2H_2O$) with 2 parts of sand and 3 parts of pyrites; the latter burns and provides the heat necessary for the reaction between the calcium sulphate and silica. Coal is thus saved and the burners may be used for lead or copper ores. Alternatively the mixture may be placed on a coking hearth and air injected. A copious current of SO_2 is thus obtained.

J. Auzies (Fr. Pat. 420,675, 1910) obtains sulphuric acid by heating anhydrous calcium sulphate with ferric oxide : $3Ca\,SO_4$ (408 kilos) + Fe_2O_3 (148 kilos) = $Fe_2(SO_4)_3 + 3CaO$, and at temperatures between 800° and 1500°, the following dissociation occurs : $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_2 + 3O$. When this gaseous mixture is passed over manganese dioxide or oxide of tungsten or molybdenum at 200°, SO_3 is obtained.

Basset (France) proposes to obtain directly from gypsum both sulphuric acid and Portland cement by heating in revolving cement furnaces (*see* Cement) a mixture of gypsum, clay, and coal made into a paste. Clinker cement is thus obtained, and the gases, containing 6·5 per cent. SO_2, pass to the lead chambers.

Although this process was tried in 1913 in the works of the Lavocat Company at Dennemont (near Nantes), doubts concerning it are justifiable when it is remembered that 50 kilos of coal are required to make 100 kilos of cement in this way.

containing 93·5 per cent. of H_2SO_4; sp. gr. 1·837) is made by concentrating in large glass retorts, 90 cm. high and of 50 cm. diameter, which are heated by gas in suitable furnaces, and an acid containing 91 to 92 per cent. of H_2SO_4 is thus obtained. In order to obtain 94 to 96 per cent. acid, iridio-platinum pans containing 10 per cent. of iridium are still used. Gilded platinum pans are still better as they are much less attacked, but these sometimes cost more than £4000.

These plants have now lost their importance, and are being gradually sold, because acid of a high degree of concentration is to-day easily and economically prepared by adding fuming sulphuric acid (oleum) to dilute chamber acid, or other more economical processes of preparing 93 per cent. acid may be used. This change is due also to the fact that during the last few years the price of platinum has risen very greatly (to more than £240 per kilo). Alloys of 90 per cent. of gold with 10 per cent. of platinum have even been resorted to. For very large plants the Negrier process (1892) has given good results. The necessary plant is shown in Fig. 116 and consists of a series of porcelain capsules or vessels disposed two by two along a kind of staircase in a furnace, resting on asbestos sheets and surrounded by sand. A current of hot air passes from the base to the top of the staircase, whilst the acid descends slowly from the top to the bottom from vessel to vessel, gradually becoming more concentrated and finally passing through a coil where it is cooled. The steam and small quantities of acid vapour are collected in a tube at the top and condensed. During the last few years the porcelain capsules have been replaced by capsules of inert iron or quartz. After some time, however, the latter develops very small cracks, through which acid escapes. 15 kilos of coke are used as fuel for every 100 kilos of 93 per cent. acid produced. In 30 vessels 90 cm. high and 40 cm. wide 2 tons of acid may be concentrated in twenty-four hours. If an acid of 97 per cent. H_2SO_4 is produced, the consumption of fuel is doubled.

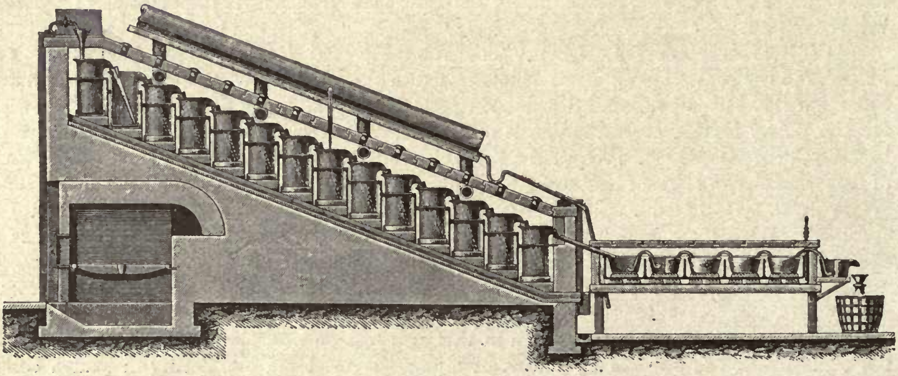


FIG. 116.

A double or treble Negrier plant for the production of 10 tons of 93 per cent. acid per twenty-four hours costs about £880.

During the last few years the Kessler process (1894) has also been extensively employed and enables commercial acid of 66° Bé. to be obtained by hot-air concentration. Hot gases from a coke producer pass in through a cast-iron pipe, *b* (Fig. 117), and are drawn along several flues, *q*, made of pumice (Fig. 118), which are hydraulically sealed by the surface of the acid, by means of an air injector, and after having traversed the surface slowly they pass, charged with water vapour and a small amount of acid vapour, through canals, *q′*, at a temperature of 150° into a kind of rectifying apparatus formed of three perforated stoneware plates, on which are placed numerous inverted porcelain capsules with their rims dipping into the acid liquid condensed on the surface of the plates. Above these plates there are two others of perforated lead, and these also support similar but smaller inverted capsules.

The acid from the lead chamber passes in through the tube *x* above, and descends in an opposite direction to the stream of gas and vapours coming from below. The almost cold gases containing much water vapour and a little acid vapour are then drawn off into the tube *h*, and are passed through a coke tower where the vapours are completely condensed. The flues, *q*, are now often advantageously constructed of simple transverse walls of volvic stone, against which the waves on the acid caused by the movement of the current of hot gases impinge, thus accelerating the concentration. Corrosion of the air aspirator may be avoided either by injecting the air or by helping it with an iron fan placed at the end—beyond the coke tower.

In all systems of concentration, the aspiration and circulation of the gas are effected more rationally and more economically by means of the new high-pressure hard lead fans devised by Paul Kestner (Lille); these are placed at the midpoint of the plant, *i. e.*, between the regenerator and the coke tower or chamber. Whereas in a large plant the steam and air injector consumes about 900 kilos of coal and the final fan beyond the coke tower requires 8 to 10 h.p. and a suction of 30 to 40 mm. of water is obtained, the Kestner fan consumes only 200 kilos of coal per day (4 h.p.) and gives a suction as high as 200 mm.

By means of the ordinary Kessler system 100 kilos of acid of 66° Bé. (92%) may be obtained with a consumption of 9 to 10 kilos of coke in the producer, and 2 to 3 kilos of coal to work the pump.

The power required is about half a horse-power per ton of acid produced. During the last few years the process has been still further improved, and a plant for the production of 10 tons of 93 per cent. acid per day costs about £1120. 98 per cent. acid may now also be produced by this process, but the production is then halved and the consumption of fuel doubled.

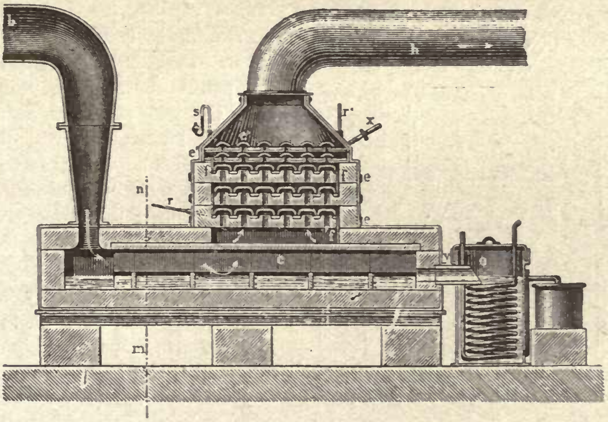


FIG. 117.

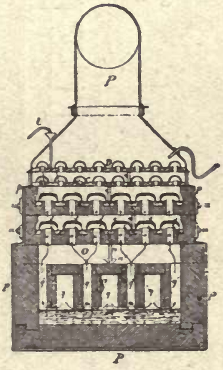


FIG. 118.

Concentrated sulphuric acid may generally be clarified, and any dark colour may be lessened by passing it through a coke filter.

An industrial concentrating plant for the production of 10 tons of sulphuric acid of 66° Bé. (93 per cent. H_2SO_4) per twenty-four hours costs from £800 to £1600 complete, and should pay for itself in twelve to fifteen years. Since 1908 the system of Gaillard of Barcelona (Eng. Pat. 23,841) has been extensively used throughout Europe for the concentration of sulphuric acid, and in 1909 there were already 100 such plants working. Sulphuric acid of 50° to 60° Bé., previously filtered through silicious sand, is made to fall in the form of a very fine spray from the top of a tower of volvic lava as much as 15 metres high and more than 3 metres in diameter, and a current of hot gases from a coke generator is passed in the contrary direction from below. Water from the dilute acid evaporates and escapes at the top together with the gases at a temperature of 150° to 160°, whilst an acid collects at the base of the tower which has a strength of 92 to 97 per cent. of H_2SO_4 according to the fineness of the spray produced. A production up to 10 tons per twenty-four hours is thus obtained. With forced draught and with perfect pulverisation of the acid, the output in a given tower has been doubled and even trebled. The gases which escape from the top of the tower descend again through a large lead pipe to enter the bottom of a small leaden tower 8 metres high and about 1·35 metres in diameter, filled with coke (more than 10 tons, in lumps the size of nuts) in order to recover the acid carried over by the current of gas and amounting to 2 tons of 40° Bé. Before being allowed to escape into the air the gases pass through a leaden box full of coke where half a ton of acid of 14° Bé. is condensed. The gases are drawn through the whole apparatus by means of a fan. Fig 119 illustrates diagrammatically the arrangement of the apparatus. *k* is the coke gas-producer and costs about £48; *T* is the concentrating tower and costs about £1040, including the patent rights; the tower, *R*, and the chamber containing coke, *kk*, together cost about £280. The fan, *V*, acid elevators, pipes, etc., cost £160, so that the complete plant costs £1520. The consumption of fuel for the concentration of the acid from 52° to 66° Bé. (92 per cent. H_2SO_4) is 12 to 14 kilos of coke per 100 kilos of concentrated acid obtained; if concentration to 96 per cent. is desired, the amount of coal used rises to 18 kilos (20 kilos with the Kessler process). The consumption of power for raising the acid is estimated at three-quarters of a horse-power per hour per ton of concentrated acid produced. The blocks of volvic lava forming the tower are cemented together with a mixture of pulverised volvic lava and sodium silicate. The tower is covered outside with sheet lead, since a little acid always percolates through the stone; it is now proposed to replace the lava with technical and economical advantage by a material called *obsidianite*, which is a vitreous silicate. In U.S. Pat. 909,578, Gaillard perfected the production of acid spray by collecting the acid not converted into spray on a conical disc placed at a definite height in the tower and removing it; he passed compressed air into the gas producer and with a larger volume of hotter gases he was able to raise the capacity of the towers from 12 to more than 30 tons.

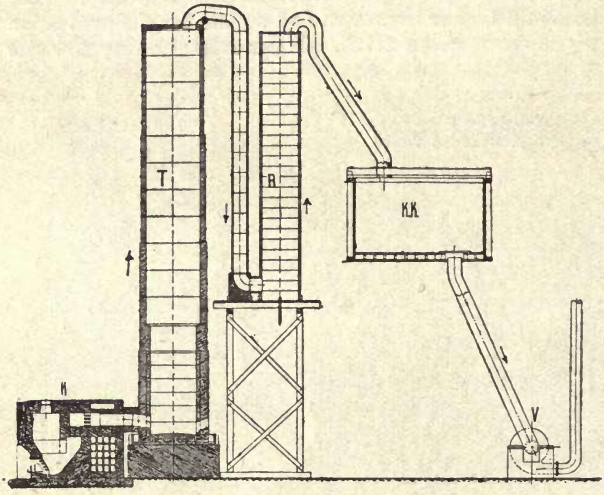


FIG. 219.

In 1912 Gaillard replaced the second tower, *R*, by a volvic stone chamber, on to the rimmed edge of which the acid to be concentrated is delivered. This acid enters the chamber through orifices, the gases being washed and cooled by the acid and the latter thus pre-heated before being forced under air-pressure in an acid egg to the pulveriser at the top of the tower.

Krell, in 1907, managed to concentrate acid to 63° Bé. in special leaden pans without the lead being attacked even at such high temperatures. The final concentration is carried out in inert iron or silicious cast-iron pans (tantiron, etc.) which resist boiling concentrated acid very well. When an acid of 66° Bé. is required the purity of which is not of great importance, concentration may be economically effected by passing the dilute acid of 50° to 60° Bé. in a fine stream into a closed pan of cast-iron in which a large amount of boiling acid at 66° Bé. is already present; water evaporates and acid of 66° Bé. is continuously removed below. The pan is changed once a year.[1]

---

[1] For some years Otto Proelss (U.S. Pat. 963,175, 1910) has successfully concentrated sulphuric acid by means of three Glover towers. One acts as an ordinary denitrating tower, being charged at the top with the dilute "nitrous" acid from the chamber whilst the furnace gases pass upwards from the bottom. The acid collected at the base has undergone concentration to 60 to 62° Bé. and is subjected to partial cooling and then pumped to the top of the second Glover tower, up which passes a portion of the gases direct from the furnaces. The walls are suitably cooled and proper regulation of the flow of acid results in the collection of acid of 66° Bé. (93·5 per cent. H_2SO_4) at the bottom; this is then cooled.

The gases issuing from the top of the two towers pass in at the top of a third Glover tower and descend together with a spray of cold dilute chamber acid; they are drawn off by means of an aspirator and sent, at the proper temperature, into the lead chambers. To avoid the deposition in the second tower of the ferric sulphate always present in acid made by any process (this becomes insoluble when the concentration exceeds 64° Bé.) towers 1 and 2 are interchanged at intervals, the more dilute acid of the denitrating tower dissolving the ferric sulphate.

The preparation of *sulphuric acid monohydrate* has already been described on p. 291, although it is to-day prepared by mixing concentrated acid of 66° Bé. with the necessary quantity of fuming sulphuric acid of known strength.

Strong sulphuric acid may be stored and despatched in wrought-iron vessels.[1]

PURIFICATION OF H_2SO_4. Purification is necessary when concentrated sulphuric acid is to be prepared. The sulphuric acid of the Glover tower is more impure than that from the chambers, and contains considerable quantities of arsenic. The more common impurities in chamber sulphuric acid are nitrosylsulphuric acid, lead, copper, iron, lime, alumina, arsenic, N_2O_3, HNO_3, ammonium sulphate, SO_2, organic substances, and sometimes selenium, tellurium, and HF. The greater part of the impurities is deposited spontaneously, and special methods are required only for the separation of arsenic and of N_2O_3. The arsenic is separated by means of hydrogen sulphide obtained from iron sulphide and H_2SO_4, about 0·2 ton of iron sulphide being required for the purification of 10 tons of chamber acid.

The crude sulphuric acid must be diluted to 46° to 50° Bé., as otherwise the H_2S is decomposed: $H_2SO_4 + 3H_2S = 4H_2O + 4S$; moreover the arsenic must be present as arsenious acid and not as arsenic acid (if necessary SO_2 must be passed through the liquid).

The operation is conducted in a Schwarzenberg tower, into the base of which a current of H_2S is passed, and down which the acid to be purified descends over acid-proof material. The acid is then passed into leaden vessels where the arsenic sulphide is deposited together with other metallic sulphides and selenium. The clear liquid is then decanted from the residue and filtered through asbestos fabrics or through porous earthenware plates under pressure. Use may also be made of a counter-current apparatus as in the "standards" used for washing illuminating gas (*see* Vol. II.).

According to the United Alkali Company (Eng. Pat. 16,929) arsenic may be separated by adding the necessary quantity of HCl and then passing a current of air through the liquid, by which means it is separated as arsenious chloride. Morange in 1908 proposed to separate arsenic by freezing acid of 63·5° Bé., as the arsenic then remains in the part which is not solidified.

G. Bressanin (1911) eliminates arsenic by adding a few c.c. of hydriodic acid to the sulphuric acid diluted to 50° Bé. and filtering through asbestos and again concentrating the acid; the excess of iodine is thus expelled.

To remove iron (fron acid to be used for making pure organic acids, such as tartaric, citric, and oxalic acids, cream of tartar, etc.), sulphuric acid of 66° Bé. is diluted with double its weight of water and then treated with a concentrated aqueous solution of potassium ferrocyanide (about 4 kilos of the salt per 1000 kilos of conc. acid), left to stand and afterwards decanted off or filtered through asbestos fabric.

In order to obtain sulphuric acid absolutely free from As, it is necessary to prepare it directly from sulphur.[2]

The nitrous compounds are separated on heating, according to Pelouze, by means of 0·1 to 0·5 per cent. of powdered ammonium sulphate, nitrogen being immediately evolved: $N_2O_3 + 2NH_3 = 3H_2O + 4N$.

Chemically pure acid is obtained by repeatedly distilling the pure concentrated acid and adding a little chromic acid in order to transform any traces of arsenious acid into arsenic acid, which does not distil. For accumulators very pure acid is required.[3]

---

[1] Even acid of 60° Bé. from the Glover tower may be stored in large wrought-iron tanks, and the larger they are the more convenient. Some are made of cylinders 3 metres in diameter and 5 metres high, but better results are obtained with cylinders 8 to 10 metres in diameter and 10 or more metres high.

[2] Sulphuric acid which is to be used for the preparation of foodstuffs, such as pressed yeast, for the fermentation of molasses, the revivification of carbon for sugar refineries, for pharmaceutical products, etc., should always be free from arsenic. Such acid is easily obtained to-day by diluting fuming sulphuric acid (oleum), which is free from impurities.

[3] **Sulphuric Acid for Accumulators.** In this acid the following substances are injurious: iron, chlorine, nitrogen, arsenic, antimony, bismuth, cadmium, copper, tin, and organic matter. The iron is usually present in organic combination and diminishes the conductivity of the plates, oxides of iron exerting an inverse reaction. Iron is determined by means of permanganate in presence of potassium thiocyanate; with an old acid not more than 0·1 per cent. of iron, calculated on the monohydrate, is allowable.

The presence of chlorine in accumulator acid leads to the formation of perchloric acid which

ANALYTICAL CONTROL OF SULPHURIC ACID MANUFACTURE. The quantity of sulphur in pyrites is determined by dissolving, for instance, 0·5 grm. in 10 c.c. of a mixture of 3 parts of concentrated HNO_3 and 1 part of HCl, and evaporating to dryness several times with HCl in order to remove any excess of HNO_3. The residue is finally dissolved in dilute HCl. The iron is precipitated with ammonia in the hot, filtered and well washed, and the sulphuric acid in the filtrate (derived from the sulphur) is precipitated with barium chloride. The weight of barium sulphate after washing, drying, and igniting gives the weight of sulphur in the sample on multiplying by 0·1373.

Copper in pyrites is determined electrolytically in a solution of the pyrites in nitric acid.

The sulphur dioxide in the gas from the pyrites burners is determined by passing a given volume of the gas through standard iodine solution: $(SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI)$.

The quantity of oxygen in the gases escaping from the last lead chamber is determined by the usual volumetric methods, that is, by absorbing the oxygen with an alkaline pyrogallate in the Bunte or Orsat burette (*see* section on Fuels).

The quantity of nitrous acid in the nitrous sulphuric acid and also in chamber acid is determined by adding the acid under examination from a burette to a given volume of a standard solution of potassium permanganate until this is decolorised; 16 parts of oxygen correspond with 47 parts of HNO_2 (*see* preceding equations: nitrous acid). The total nitrogen (that is, HNO_3 and HNO_2) is determined with Lunge's nitrometer (*see* section on Sodium Nitrate). The strength of sulphuric acid is ordinarily determined by means of its density (*see* Table, p. 286), but in the case of very concentrated acid it is necessary to determine it by titration, after previous dilution, with standard sodium hydroxide and methyl orange, which is coloured red by strong acids.

YIELDS. Theoretically 100 kilos of sulphur should give 200 kilos of SO_2, 250 kilos of SO_3, 306·5 kilos of H_2SO_4 monohydrate, 319 kilos of sulphuric acid of 66° Bé. (96 per cent. H_2SO_4), or 490 kilos of chamber sulphuric acid of 50° Bé. (62·5 per cent. H_2SO_4).

With pyrites burners 10 to 12 per cent. of the sulphur was at one time lost (part remained in the burnt pyrites) and the consumption of nitrate was also very great. To-day the total loss of sulphur has been reduced to from 4 to 5 per cent., and the consumption of nitrate is 2 to 3 per cent. of the sulphur burnt;[1] the nitre is now advantageously replaced

---

energetically attacks the lead plates, whilst the oxidation leads to loss of energy. Chlorine is tested for by means of silver nitrate; not more than 0·02 per cent. Cl, referred to the monohydrate, is permissible.

Nitrogen occurs as ammonia and is tested for with caustic soda and Nessler solution; not more than 0·1 per cent. N, calculated on the monohydrate, should be present.

Of other metals, arsenic is the most harmful, as it gives arsenic acid, which attacks the lead plates and connections; it is detected by means of H_2S.

Among organic compounds, alcohol and acetic acid are somewhat harmful.

Only distilled water and pure sulphuric acid should be used for accumulators. The above tests are made on the acid after dilution with distilled water.

Purification of acid for accumulators. The acid is used at about 22° Bé. or 34° Bé. Use may also be made of acid of 40° Bé. from the third lead chamber, this being less impure than that of the first and second chambers. After dilution to the required degree and, if necessary, after filtration, the acid is treated with 40 to 50 c.c. of barium sulphide solution of 7° Bé. per 50 to 60 litres of the acid. The whole is mixed and allowed to stand until hydrogen sulphide is no longer evolved (1 to 2 days). All the metallic impurities are thus deposited in a finely divided state and after prolonged rest the pure acid is decanted off. To test its purity, a little of the acid is treated in a test-tube with a scrap of chemically pure zinc; with pure acid no action occurs, but with impure acid hydrogen is evolved after a few minutes, even minimal traces of impurities acting as catalysts.

[1] The loss of nitrate is shown by the quantity which it is necessary to add to the nitre pots each day to make up for losses. In the case of lead chambers of small capacity, that is, those in which the working is very intense compared with the amount of sulphur or pyrites burnt (2 kilos of Spanish pyrites per cubic metre of chamber space per twenty-four hours), more nitrate is consumed (up to 4 kilos per 100 of sulphur), whilst in chambers of ample dimensions and less intense production 2 per cent. of nitrate is used on the sulphur burnt; the nitrate which circulates in the whole system of chambers and towers is about 12 to 15 per cent. of the sulphur burnt. The loss of sulphur was, on the average, 50 per cent. in 1820, 20 per cent. in 1850, 14 per cent. in 1880, 8 per cent. in 1890, and 4 per cent. in 1914. The mean consumption of nitre (expressed as nitric acid of 36° Bé.) was 12 kilos per 100 kilos of sulphuric acid of 50° Bé. in 1820, 6 kilos in 1850, 3 in 1880, 1·5 in 1890, and 0·6 in 1914.

by nitric acid of 25° to 36° Bé. and the consumption of nitric acid may be reduced even to 0·5 kilo per 100 kilos of sulphuric acid of 60° Bé.

Yields of acid per volume of chamber space have already been mentioned in connection with tangential chambers on p. 298.

COST OF PLANT AND PRODUCTION. Lunge gives the following estimate of the cost of a Niedenführ plant with a production of 20 tons of H_2SO_4 per twenty-four hours, that is, with the corresponding production of chamber and Glover acid.

The gases from 12 burners burning lump pyrites pass through the dust flues and then into the base of the Glover tower, and pass out at the top through two large pipes into the neighbouring lead chamber at the top. The gases escaping from this chamber pass through three openings at its base in the opposite wall, and then pass through a single large leaden pipe into three openings in the top of the second lead chamber, which is close to and parallel to the preceding one. They pass through this chamber in the same way and the issuing gases escape at the base of the opposite wall through three openings and arrive at the third chamber, passing from the opposite wall of this chamber into two Gay-Lussac towers which are placed close to the Glover tower. The remaining gases escape directly into the air. Each of the three chambers is 8 metres high and 32 metres long and together they have a volume of 8800 cu. metres.[1]

APPENDIX TO THE SECTION ON SULPHURIC ACID

THEORY OF THE FORMATION OF SULPHURIC ACID IN THE LEAD CHAMBERS. In 1913 B. Briner and A. Kühne showed that a mixture of $SO_2 + NO_2$ may yield SO_3 and this with water H_2SO_4, so that the process may be summarised in the single principal reaction, $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$; all the other reactions which have been discussed for so many years must be secondary or abnormal reactions.

STATISTICS. The production in the United States, shown on p. 285, is classified as follows: 915,000 tons at 50° Bé., 380,000 at 60° Bé., and 675,000 at 66° Bé.[2] The output in Italy in 1915 was 626,000 tons, of the value £1,120,000.

---

[1] The prices of materials in this estimate refer to the year 1902:

		£
I.	Freehold, 25,000 sq. metres at 2*s*.	2500
II.	Walls, pavements, foundations, wooden framework and sheds for the furnaces, chambers, boilers, towers, etc.	3800
III.	Boilers (40 sq. metres heating surface), pumps, pipes, acid elevators	750
IV.	Twelve burners for lump pyrites, dust flues, nitre pots, and connection with Glover tower	1124
V.	Chambers and towers: 240 tons of lead, material for filling towers and cost of complete erection (estimated at £1320)	6326
	Total	£14,500

Later (*see* Sulphur Trioxide), comparisons will be made between the cost of the acid produced by such a plant and a more rational plant with five rotary furnaces, two lead chambers, five plate-towers, one Gay-Lussac tower, and one Glover tower for the daily production of 20 tons calculated as monohydrate. It would, however, appear that in the above estimate Lunge has taken an extremely exaggerated price for land and too scanty an area.

[2] On the occasion of the Eighth International Congress of Applied Chemistry at New York (October, 1913) a visit was paid to the largest sulphuric acid works in the world, that of the Tennessee Copper Co. at Ducktown. Use is there made of 75 % of pyrrhotite (nFeS + FeS_2, with 38–40 % S) and 25 % of pyrites with a mean content of 2 % of copper, which is recovered by working the ore in seven large furnaces, from which a fused regulus containing 15 % Cu is obtained. The gases, which are somewhat dilute and contain 4–5 % of CO_2, pass into an immense dust chamber 11 metres wide by 8 metres high by 50 metres long, and thence to two octagonal Glover towers 15 metres high and 9 metres in diameter with nitre pots at the foot. The gases are then led along a channel 3 metres high, 6 metres wide, and 37 metres long, and are drawn by means of four hard lead fans (capacity 1900 cu. metres of gas per minute) through 24 cooling chambers (3·3 metres high, 3·1 metres wide, and 21 metres long), to be introduced into a series of 26 lead chambers of the Falding type (*i. e.*, very high) and of the dimensions

In the Argentine in 1910 there was only one important sulphuric acid works (at Buenos Ayres), producing 1500 tons of acid, the importation being 1600 tons.

In 1913 Belgium contained 26 sulphuric acid works with 400,000 cu. metres of lead chamber, and, of the acid produced, about 90,000 tons (calculated at 60° Bé.) were exported to Germany, the remainder being used in superphosphate works.

In 1914 there were in Germany 4,000,000 cu. metres of lead chambers, and the acid produced in 1912 was obtained from 981,556 tons of pyrites, 554,760 tons of zinc blende, 44,481 tons of lead and copper sulphides; from Laming mixture from gas-works 35,500 tons of sulphuric acid were produced. In two dyestuff factories alone 300,000 tons of the acid are consumed per annum.

In England there were 200 sulphuric acid works in 1911. India imported 4000 tons of sulphuric acid in 1912, and the erection of a large works was started at Bombay in 1913.

SULPHUR TRIOXIDE AND FUMING SULPHURIC ACID

I. SULPHUR TRIOXIDE : SO_3

Until about 1875 the sulphur trioxide of commerce was prepared only by Starck, of Prague, who obtained it by distilling fuming Nordhausen acid. In 1875 Cl. Winkler, who was followed by Squire and Messel, showed that sulphur trioxide is easily formed by the interaction of SO_2 and O in presence of very finely divided platinum, which acts catalytically without taking any direct part in the reaction.[1]

In this process 20,600 cals. are developed, and the maximum yield is obtained between fixed temperature limits, as otherwise the SO_3 is dissociated, regenerating $SO_2 + O$.

---

15 × 15 × 20 metres, so that the total value is 130,000 cu. metres. Lastly come 10 Gay-Lussac towers with base 7 × 7 metres and 16 metres high. The acid tanks number 15, each of 1000 tons capacity, and the lead used for the chambers and towers amounts to 3600 tons. The annual output of acid is 180,000 tons of 60° Bé.

As regards the tower chambers mentioned in the Note on p. 306, various plants of this type are in use in different countries. A system of six towers of 3 metre side and 12 metres high produces daily 18 tons of acid of 60° Bé., about 12 tons of pyrites being burnt, and 0·9 % of nitric acid of 36° Bé. consumed, in the 24 hours. The towers are filled with rings of sandstone or coke, the reaction being thereby accelerated (20 minutes instead of 5 hours in the chambers). With two parallel rows, each of three towers, tower 1 receives the nitrous acid from tower 6, tower 2 that from tower 5, and tower 3 that from tower 4; the acid is raised with Mammoth pumps (air-emulsion, *see* p. 303) and cooled by means of water in the lift pipes. The gas entering the first tower at 360–400°, passes to tower 2 at 60°, to tower 3 at 56°, to tower 4 at 40°, to tower 5 at 36°, and to tower 6 at 30°. The acid made is of 55–60° Bé. The power required for four mechanical furnaces is 2·5 kilowatts, while the gas aspirator absorbs 1·5 kilowatts; the Mammoth pumps consume per day 4000 cu. metres of air at 2 atmos. Two workmen are required for the four burners and one for the six towers. The latter have a total volume of 600 cu. metres and produce 30 kilos of acid at 60° Bé. per cu. metre per 24 hours. If these six towers (without burners and without erection) cost £4800 (£8800 with burners and erection), a lead chamber plant of similar capacity would cost £14,800 (including burners and erection). These tower chambers were improved by G. Schliebs (1914), the mixing and cooling of the gas being rendered more thorough. An acid separator is applied to each tower and a system of communicating pipes between the towers permits of the circulation of the gas from any tower; in this way less acid is circulated through the towers and the oxides of nitrogen are well utilised.

According to H. Klencke (Ger. Pat. 284,995, 1913) a marked advantage—as in the Glover towers—should ensue by drawing the gases rich in SO_2 from the top to the bottom of towers down which the more concentrated "nitrous" acid falls; in this way the contact of the gaseous reagents is prolonged and the condensation of the sulphuric acid gradually forming facilitated.

[1] It was found afterwards that the oxides of iron, chromium, manganese, copper, and cobalt also react less completely, and that metallic gold, palladium, iridium, silver, iron, quartz, glass powder, pumice-stone, burnt clay, bricks, etc., all act as catalysers in the hot and when finely subdivided.

This method of Winkler has attained important industrial application only during the last few years, and by means of SO_3 pure sulphuric acid of any concentration is now industrially prepared.

SO_3 was formerly also obtained by decomposing strong sulphuric acid in contact with retorts heated to redness (Debray and Deville's process, *see* p. 195). The mixture of $SO_2 + O + H_2O$ (steam) so obtained was dried in a coke-tower with strong sulphuric acid and the mixture of $SO_2 + O$ passed over platinised clay balls, the reaction $SO_2 + O = SO_3$ then occurring.

Sulphur trioxide may also be prepared by heating sodium pyrosulphate, $Na_2S_2O_7$, which is prepared by heating sodium sulphate with strong sulphuric acid: $SO_4Na_2 + H_2SO_4 = H_2O + S_2O_7Na_2$; acid sodium sulphate, $NaHSO_4$, is formed as an intermediate product, and when heated is transformed into the pyrosulphate. By adding a further quantity of sulphuric acid and distilling *in vacuo* sulphur trioxide is obtained: $S_2O_7Na_2 + H_2SO_4 = 2SO_4HNa + SO_3$. The two molecules of bisulphate formed are reconverted into pyrosulphate. Sulphur trioxide is also obtained on heating sodium pyrosulphate directly to 600°: $Na_2S_2O_7 = Na_2SO_4 + SO_3$.

Prud'homme (1909) decomposes various sulphates in the electric furnace and thus obtains SO_3 and metallic oxides: thus from calcium sulphate $CaO + SO_3$ are obtained. R. Frank (1906, Ger. Pat. 194,879) says that SO_3 is formed quantitatively without the presence of a catalyst when $SO_2 + O$ are heated at a pressure of 100 atmospheres.

In the laboratory SO_3 is obtained by heating fuming sulphuric acid, which is merely a solution of SO_3 in strong sulphuric acid, and condensing the vapours of SO_3 in a cooled receiver.

It may be prepared also by distilling concentrated sulphuric acid with phosphorus pentoxide in a retort: $P_2O_5 + H_2SO_4 = SO_3 + 2PO_3H$ (metaphosphoric acid).

White fumes are thus formed which condense to a white crystalline silky mass in a receiver surrounded by ice.

PROPERTIES. The needle-shaped crystals of SO_3 melt at 16·8° (Lichty, 1909), yielding an oily liquid of sp. gr. 1·96 (at 20°), which distils at 44·88° (760 mm.) without dissociation. Its coefficient of expansion between 15° and 20° is 0·002005.

If pure it can be preserved unaltered, but it absorbs moisture with avidity from the atmosphere forming H_2SO_4, traces of which slowly transform it into a white solid mass like asbestos which melts at 50° and appears to be polymerised SO_3. On re-distilling this mass pure SO_3 is again obtained.

It combines violently with water to form sulphuric acid, producing a strong hissing sound, and sometimes even an explosion if a comparatively small quantity of water is present. Its avidity for water is such that it decomposes almost all hydrogenated organic substances, acquiring a brown colour. When heated in red-hot tubes it decomposes into $SO_2 + O$. The quality found in commerce (*see below*, Fuming Sulphuric Acid) contains 98 to 99 per cent. of SO_3 and 1 to 2 per cent. of H_2O; it is to-day preferred dissolved as a liquid in a small amount of sulphuric acid, namely, with 87 to 92 per cent. of total SO_3 = 30 to 60 per cent. of free SO_3. It is then called *oleum* or *fuming sulphuric acid*, and is stored and despatched in wrought-iron vessels.[1]

---

[1] When the anhydride contains 1 per cent. of water, the latter is not free but combined in the form of H_2SO_4, with which it forms 5·44 per cent., so that 94·56 per cent. of free SO_3 is really present in the mixture. In the same way, when 5 per cent. of water is present this is in the form of 27·2 per cent. of H_2SO_4, while 72·8 per cent. of free SO_3 is present. The strength or percentage of commercial oleum is indicated by the percentage of free SO_3. The qualities ordinarily used contain from 25 to 45 per cent., that is, 25% to 45% of free SO_3 or 95 per cent. of total SO_3. The strength of these liquids is also often given in terms of monohydrate (22 per

On pouring a little sulphur into sulphur trioxide it dissolves, forming a bluish-green substance which is actually sulphur sesquioxide, S_2O_3. W. Traube (1913) found that dry SO_3 vapour is slowly fixed by certain dry salts ; thus, NaCl gives NaCl S_2O_6 (sodium chloropyrosulphate), while $NaNO_2$ yields $NaNO_2$ $(SO_3)_3$ (sodium nitrosotrisulphonate). With persulphates, $2SO_3$ condenses.

The heat of formation of SO_3 from $SO_2 + O$ is equal to 86 Kj. (20,600 cals.), and since SO_2 obtained from sulphur and oxygen has a heat of formation of 297 Kj. (= 70,977 cals.) we may deduce a total heat of formation of sulphur trioxide from its elements $S + O_3$ of 383 Kj. (= 91,577 cals.). From these thermochemical data we see that the law of Berthelot, according to which the reacting substances form by preference new substances with a maximum development of heat, is untrue in this case, because on burning sulphur in oxygen

---

cent. of free SO_3, corresponding with 105 per cent. of monohydrate). The following table of strengths is useful :

DENSITIES AND CONCENTRATIONS OF OLEUMS

Density at 35° C.	100 parts by weight correspond with				Density at 35° C.	100 parts by weight correspond with			
	SO_3		H_2SO_4 (monohydrate)	Sulphuric acid of 50° Bé.		SO_3		H_2SO_4 (monohydrate)	Sulphuric acid of 50° Bé.
	Total	Free				Total	Free		
1·8186	81·63	0	100·00	160·00	1·9749	91·18	52	111·70	178·72
1·8270	81·99	2	100·45	160·72	1·9760	91·55	54	112·15	179·44
1·8360	82·36	4	100·90	161·44	1·9772	91·91	56	112·60	180·16
1·8425	82·73	6	101·35	162·16	1·9754	92·28	58	113·05	180·88
1·8498	83·09	8	101·80	162·88	1·9738	92·65	60	113·50	181·60
1·8565	83·46	10	102·25	163·60	1·9709	93·02	62	113·95	182·32
1·8627	83·82	12	102·70	164·32	1·9672	93·38	64	114·40	183·04
1·8692	84·20	14	103·45	165·04	1·9636	93·75	66	114·85	183·76
1·8756	84·56	16	103·60	165·76	1·9600	94·11	68	115·30	184·48
1·8830	84·92	18	104·05	166·58	1·9564	94·48	70	115·75	185·20
1·8919	85·30	20	104·50	167·20	1·9502	94·85	72	116·20	185·92
1·9020	85·66	22	104·95	167·92	1·9442	95·21	74	116·65	186·64
1·9092	86·03	24	105·40	168·64	1·9379	95·58	76	117·10	187·36
1·9158	86·40	26	105·85	169·36	1·9315	95·95	78	117·55	188·08
1·9220	86·76	28	106·30	170·08	1·9251	96·32	80	118·00	188·80
1·9280	87·14	30	106·75	170·80	1·9183	96·69	82	118·45	189·52
1·9338	87·50	32	107·20	171·52	1·9115	97·05	84	118·90	190·24
1·9405	87·87	34	107·65	172·24	1·9046	97·42	86	119·35	190·96
1·9474	88·24	36	108·10	172·96	1·8980	97·78	88	119·80	191·68
1·9534	88·60	38	108·55	173·68	1·8888	98·16	90	120·25	192·40
1·9584	88·97	40	109·00	174·40	1·8800	98·53	92	120·70	193·12
1·9612	89·33	42	109·45	175·12	1·8712	98·90	94	121·15	193·84
1·9643	89·70	44	109·90	175·84	1·8605	99·26	96	121·60	194·56
1·9672	90·08	46	110·35	176·56	1·8488	99·63	98	122·05	195·28
1·9702	90·44	48	110·80	177·28	1·8370	100·00	100	122·50	196·00
1·9733	90·81	50	111·25	178·00					

I. Prats (1910) gives the following formula for the dilution of oleum to any percentage of SO_3 by the addition of sulphuric acid of 66° Bé. (95·6 per cent. H_2SO_4); if we indicate the quantity in grams of more dilute oleum which is to be prepared by α, the strength of SO_3 which has to be obtained by h, and the quantity of more concentrated oleum which is used by x, its strength in SO_3 by k, and the amount of sulphuric acid of 66° Bé. to be added by y, then :

$$x = \alpha \, . \, \frac{h + 20}{k + 20} \; ; \quad y = \alpha \, . \, \frac{k - h}{k + 20} .$$

If, for example, we wish to prepare 400 grms. of oleum of 20 per cent. SO_3 from oleum containing 30 per cent. SO_2 and sulphuric acid of 66° Bé., we have the equations :

$$x = 400 \, \frac{20 + 20}{30 + 20} = 400 \, \frac{4}{5} = 320,$$

and as $y = \alpha - x$ we have : $y = 400 - 320 = 80$, that is, we must mix 320 grms. of oleum of 30 per cent. SO_3 with 80 grms. of sulphuric acid of 66° Bé. to obtain 400 grms. of oleum of 20 per cent. SO_3. This formula is just as exact as the more complex one of Gnehm.

or air sulphur dioxide is formed almost exclusively (to the extent of 95 per cent.). This fact is clearly explained by the law of mass action (*see below* and pp. 62 and 68).

Sulphur trioxide is used in coal-tar colour works, but more especially for the preparation of fuming sulphuric acid.

II. FUMING SULPHURIC ACID

This substance is also called oleum, Nordhausen acid, pyrosulphuric acid, or disulphuric acid, $HO\text{-}SO_2\text{-}O\text{-}SO_2\text{-}OH$.

It is the product of the addition of 1 mol. of sulphuric acid to 1 mol. of sulphur trioxide.

Until a few years ago it was obtained by distilling dry ferrous sulphate, which decomposes, in common with all sulphates except those of the alkali and alkaline earth metals, at a red heat according to the following equation: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. In order to avoid the formation of SO_2 the iron sulphate is oxidised by roasting it in the air. Basic ferric sulphate is thus formed which on heating forms directly 1 mol. of sulphuric acid and one of sulphur trioxide: $4FeSO_4 + O_2 + 2H_2O = 4FeSO_4(OH)$, and from this: $2FeSO_4(OH) = Fe_2O_3 + H_2SO_4 + SO_3$. The iron oxide is then employed as a red mineral pigment under the name of colcothar.

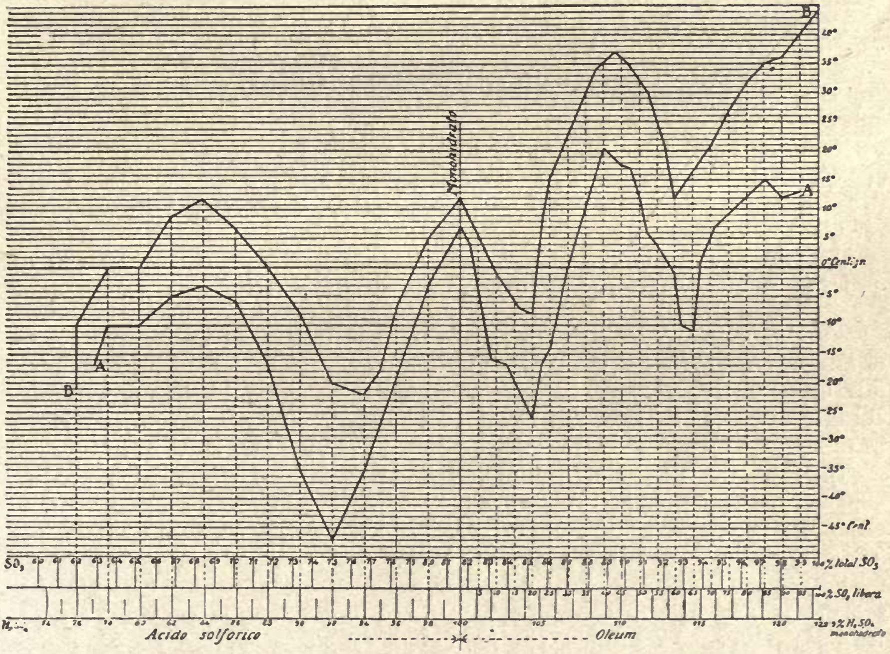


FIG. 120.

This process was already known to Arab alchemists and was applied on a large scale at Nordhausen (Prussia) during the seventeenth and eighteenth centuries. After 1792 it was prepared on an industrial scale almost exclusively by the firm of Starck in Bohemia by weathering iron pyrites in the air. Ferrous and ferric sulphates were thus formed which were extracted with water and the solution evaporated. The residue was then roasted in reverberatory furnaces, in order to obtain a product containing ferric sulphate only, and this was dry-distilled in clay retorts at a red heat: $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$.

Since the industrial preparation of sulphur trioxide by the catalytic process, fuming sulphuric acid has been prepared profitably and exclusively by saturating sulphuric acid with sulphur trioxide and comes on to the market in the name of "oleum" of various concentrations. The SO_3 is absorbed by 98·5 per cent. (or even more dilute) sulphuric acid by passing it over the surface of the acid or through the latter in closed vessels until an oleum containing 30 per cent. of SO_3 is obtained. In order to obtain a greater concentration this oleum is distilled in ordinary iron pans over direct flame, and the sulphur trioxide is then absorbed by other oleum of 30 per cent. which is kept cool. Oleums containing 60 per cent. and even 80 per cent. of free SO_3 are thus obtained. They form heavy liquids which fume in the air and are slightly brown in colour owing to the presence of dissolved traces of organic matter; traces of iron salts render it milky. The specific heat of oleum containing 24 per cent. of free SO_3 is 0·340, with 56 per cent. 0·400 and with 90 per cent. 0·652. It has a specific gravity of 1·86 to 1·95. The specific gravity is irregular, and is not always proportional to the content of free SO_3; thus, oleums containing 10 per cent. to 56 per cent. of free SO_3 have densities gradually increasing from 1·856 to 1·977, and then from 57 per cent. to 98 per cent. of SO_3, the specific gravity decreases from 1·976 to 1·840 at a temperature of 35° (*see* preceding Table).

The strength of oleum is determined by weighing a given quantity in a thin glass tube sealed in the blow-pipe and breaking this under cold water, the solution being then titrated with normal NaOH in presence of methyl orange. If any SO_2 is present this is titrated with iodine solution.

In order to detect traces of nitric acid in oleum by means of diphenylamine, the acid should be first diluted until it contains less than 20 per cent. of free SO_3 (W. N. Iwanow, 1912).

Oleum solidifies the more easily at ordinary temperatures the more SO_3 it contains and this constitutes a practical difficulty, because it is always necessary to heat it to 25° to 30° in order to liquefy it, so that liquid oleum of a strength which is not too high (20 to 25 per cent.) is preferred.

The price of oleum of about 30 per cent. of free SO_3 is £3 4*s*. to £4 per ton in large quantities and it is stored and despatched in wrought-iron vessels.

Fuming sulphuric acid is used in very large quantities in the manufacture of aniline colours and explosives, to obtain highly concentrated nitric-sulphuric mixtures; in the manufacture of phosgene from $C\,Cl_4$, in the preparation of chlorhydrin (*see later*), in the refining of mineral oils, paraffin wax, etc., and in many cases when the strength of dilute sulphuric acid is to be increased.

In 1888 the Badische Anilin und Sodafabrik of Ludwigshafen produced 18,000 tons of sulphur trioxide catalytically, and in 1900 160,000 tons. In Germany 93,000 tons of fuming sulphuric acid were produced catalytically in 1904, and about 100,000 tons in 1905. The consumption then increased rapidly in all countries. In 1911 there were 24 works making catalytic (contact) sulphuric acid in Germany, and this number was increased during the European War. In France, the St. Gobin Co. alone had at work 20 oleum plants each turning out 5000 tons per annum. In Italy before the war there were only 6 oleum plants, whilst in 1917 there were 20, 10 on the Tentelew system in the Cengio works of the Società Italiana Prodotti Esplodenti.

INDUSTRIAL MANUFACTURE OF SO_3 AND FUMING SULPHURIC ACID

This is closely connected with the manufacture of sulphuric acid, and will in all probability replace the old system of lead chambers.

It is therefore useful to explain this new and very important process in some detail. Until a few years ago the process of Hänisch and Schröder, based on the reaction proposed by Winkler in 1875, was a serious competitor of the only fuming sulphuric acid works, that of Starck (at Prague), who obtained it by distilling ferrous sulphate. Hänisch and Schröder at first worked with pure concentrated SO_2, but afterwards used dilute SO_2 as obtained from the pyrites burners, bringing it into contact with the catalytic mass of hot platinised asbestos at a pressure of about three atmospheres in order to obtain more intimate contact. They thus hoped to obtain an easier reaction and a better yield. The process of Hänisch and Schröder has to-day been completely replaced by more rational catalytic processes, which are used without pressure and by which almost theoretical yields are obtained. Until 1898 the greatest secrecy was maintained on the industrial preparation of SO_3 by catalytic means.[1]

Through the indiscretion of a workman of the Ludwigshafen works, who communicated the secret to competing firms, three patents were taken out almost simultaneously by the Badische Anilin und Sodafabrik of Ludwigshafen, the Farbwerke vorm. Meister Lucius und Brüning of Höchst, and the Verein chemischer Fabriken of Mannheim.

In 1901 Knietsch, who had studied the problem for years at the Badische Anilin und Sodafabrik, and who had succeeded after many attempts in discovering the industrial solution of the problem, read a paper before the German Chemical Society at Berlin which threw a little light on this new industry.

An epoch fruitful in practical results in connection with the catalytic manufacture of SO_3 was started in 1875 by the discoveries of Clemens Winkler and of Squire and Messel. They employed platinised asbestos, containing less than 5 per cent. of platinum, and succeeded after many attempts in establishing the necessary practical conditions for obtaining an industrial yield of SO_3. They found that this catalytic substance transformed 78 per cent. of SO_2 into SO_3 when SO_2 and O were present in the stoichiometric proportions necessary to give SO_3. If, on the other hand, other gases, or even an excess of SO_2 or O, were present, they found that the yield was diminished even to 12 per cent. (this was shown later to be erroneous).

At that time Winkler, Squire, and Messel decomposed concentrated sulphuric acid by Deville's process (*see* p. 195) in order to obtain $SO_2 + O$ in the right proportions[2]; they

---

[1] In 1823 Döbereiner discovered that finely divided platinum becomes hot in presence of O and H by causing them to combine. Dulong, Thénard, Dumas, and Mitscherlich also discovered various substances which cause reactions without being altered themselves. These substances were called *catalytic* substances by Berzelius in 1836. In 1821 a vinegar manufacturer of Bristol named P. Phillips obtained an English patent, 6096, in which he stated that on passing sulphur dioxide mixed with air through a hot tube filled with platinum wire sulphuric acid was formed on dissolving the product in water, without the necessity for using nitrate or a lead chamber. The same thing happened to Phillips' discovery as happened to the ammonia-soda process discovered by Dyar and Hemming at that time in England, and to the process of mercerising cotton discovered by Lowe, also in England, in 1894; it found no application in that country, but was then studied and made into an industrial process elsewhere, although Phillips' results were confirmed in 1832 in Germany by Magnus and also by Döbereiner. In 1838 it appears that Kuhlmann had taken out a French patent of similar trend to that of Phillips. In 1847 a Belgian chemist, Schneider, prepared a small quantity of sulphuric acid by a catalytic process in a small apparatus, employing pumice prepared in a special manner (perhaps with platinum) as a catalytic substance. In 1846 Jullion (Eng. Pat. 245) proposed the use of platinised asbestos in order to obtain oxidised compounds of nitrogen or chlorine from HCl and hot air.

In 1848 Laming prepared H_2SO_4, using as catalyst pumice impregnated with manganese dioxide and a trace of ammonia at about 300°. In 1852 Wöhler and Mohla found that H_2SO_4 is obtained by employing as catalytic substance copper, iron, or chromium oxides at a red heat, and explained this fact by supposing that these oxides are transformed into lower oxides yielding oxygen; the reaction occurred also in absence of water. In 1853 Nobb, in two English patents, proposed as a catalytic substance iron oxide (burnt pyrites), which acted still better in the presence of some manganese oxide.

In 1852 Petrie proposed the use of platinised asbestos for the manufacture of sulphuric acid, and afterwards Thornthwaite (Eng. Pat. 188 of 1854) also proposed platinised asbestos in the hot for the production of H_2SO_4 by contact, or even sesquioxides of iron, chromium, and other metals. In 1855 Piria prepared sulphur trioxide from $SO_2 + O$ in presence of platinised pumice. In 1856 Petrie proposed powdered quartz as a catalytic substance, and this was tried by Hunt, by Plattner, and by Reich, but without much success. In 1871 Deacon and Hurter used as catalytic agents copper salts, which had already been used for obtaining chlorine from HCl and air, but the results were not encouraging. All attempts made up to this time endeavoured to obtain sulphuric acid, as the consumption of pure sulphur trioxide and of fuming sulphuric acid was then very small, and thus in all these experiments moisture and dust were not excluded. It is now known that these two substances rapidly paralyse the catalytic action of platinum. In 1862 Graebe and Liebermann prepared synthetic alizarine, and after that time the coal-tar colour works needed large quantities of sulphur trioxide and fuming sulphuric acid in order to prepare the organic sulpho-acids.

[2] In England the Squire process (which was patented, whilst Winkler did not patent his process in Germany) was gradually perfected in the large works of Thann of London, and,

dried the mixture of $SO_2 + O + H_2O$, in order to separate the water, and then brought $SO_2 + O$ into contact with the hot platinised asbestos. The industrial preparation of SO_3 for the manufacture of fuming sulphuric acid was thus started. Up to that time this acid was a monopoly of the firm of Starck, and prior to 1877 the price rose very greatly to as much as 2*s.* 7*d.* per kilo of SO_3 on account of the large consumption in the aniline dyestuff works. In 1879 E. Jacob, in Kreuznach, placed on the market fuming sulphuric acid (oleum), prepared by Winkler's process, obtaining a yield of 70 per cent. by using sulphuric acid of 66° Bé., which was transformed into oleum containing 43 per cent. of free SO_3.

In 1866 the Farbwerke Höchst acquired the Jacob-Winkler process, but immediately afterwards, instead of decomposing H_2SO_4, they worked with SO_2 from pyrites burners. In 1887 they found it more advantageous to burn Sicilian sulphur, which gave pure SO_2, directly.

From 1881 the Badische Anilin und Sodafabrik at Ludwigshafen also worked by Winkler's process, and afterwards by the process of Schröder and Hänisch by which reaction between the pure SO_2 and O was caused in the hot under a pressure of three atmospheres. They employed the dilute SO_2 gases from pyrites burners only later, and this allowed them to give a great impetus to this industry, as they were able to produce cheap sulphuric acid in competition with that obtained by the ordinary process in the lead chambers.[1]

The theoretical explanation of the catalytic formation of SO_3 is given by the mass law: SO_2 and O cannot be completely transformed into SO_3 because the reaction is reversible: $2SO_2 + O_2 \rightleftarrows 2SO_3$, and we must therefore apply the general formula of mass action (p. 68), $\frac{C_1{}^{n_1} \cdot C_2{}^{n_2}}{C_1'{}^{n_2'}} = K$, where $C_1 = SO_2$, $C_2 = O_2$, $C_1' = SO_3$, and where n indicates the number of molecules; we then have $\frac{(SO_2)^2(O_2)}{(SO_3)^2} = K$, whence $\frac{SO_3}{SO_2} = \sqrt{\frac{O_2}{K}}$; if therefore we wish to form larger quantities of SO_3 we must increase the concentration of the oxygen. Theoretically this greater concentration should be produced by means of pure oxygen. Practically, however, the same yield is also obtained by simply employing larger quantities of air so that the oxygen is present in excess compared with the SO_2. The yield is not appreciably influenced by the excess of nitrogen.

With a stoichiometric mixture of $2SO_2 + O_2$ at 450°, Knietsch obtained a yield of 94 per cent., and on maintaining the same relation between SO_2 and O in the form of air he obtained almost the same yield, namely, 91 per cent.

The best results have been obtained in practice when the oxygen is present in three times the quantity required by theory. The gases from the pyrites burners correspond closely with this composition, namely: $2SO_2 + 3O_2$,

---

starting with the decomposition of H_2SO_4, they finally used Sicilian sulphur for the preparation of SO_3. They thus obtained 90 per cent. of the theoretical yield of SO_3. The decomposition of the strong sulphuric acid required very high temperatures and the plant was rapidly destroyed, so that the whole process was somewhat dear. Even when burning sulphur they always maintained the stoichiometric ratio between SO_2 and O.

It was believed to be advantageous, in order to obtain a maximum yield, to have at least one of the two gases in a very pure state, and they then (after 1880) used the process of Schröder and Hänisch, which gave pure SO_2, and also used pure electrolytic oxygen. It was only later, by applying the law of mass, that the process was facilitated and completed by increasing the amount of one of the reacting gases.

[1] The attempts to obtain cheap SO_2 directly from pyrites burners date from 1878 and were always kept secret both in the works of Muldener, of Frieberg, who worked by Winkler's process, and in that of Thann, of London, where Squire's process was employed. In 1900 Winkler published the history of all these experiments and mentioned the great difficulty encountered in purifying the gas from the pyrites burners, which readily paralysed the catalytic action of the platinum, and stated that it was Jacob (*see above*) who solved the difficulties by burning sulphur instead of pyrites. In 1883 Rath purified the gases from the pyrites burners by first cooling them and then drying them in a tower with a spray of strong sulphuric acid. The gaseous mixture was then suitable for the catalytic reaction.

because they contain 7 per cent. of SO_2, 10 per cent. of O_2, and 83 per cent. of N_2 by volume.

According to the law of mass action the yields should be improved by increasing the pressure, but in practice no advantage is so obtained.

Knietsch found experimentally that the most favourable temperature for the catalytic reaction is from 400° to 450°; a yield of 99 per cent. of SO_3 compared with the SO_2 present is thus obtained. At higher temperatures the SO_3 decomposes rapidly and at 1200° decomposition is complete if the heating occurs out of contact with the catalytic material; in presence of the catalytic material the decomposition occurs at lower temperatures, so that even at 1000° no SO_3 is formed in presence of platinum.

The decomposition of the SO_3 depends on the temperature alone, and thus proceeds equally rapidly whatever may be the catalytic substance. Consequently only those catalytic substances should be suitable which exercise their maximum catalytic effect at a temperature below 450° (that is, between 200° and 450°), whilst other catalysers, which act at higher temperatures, should give a lower yield. Platinum satisfies these conditions, whilst iron oxide, which is also used industrially as a catalyst, acts at higher temperatures and does not give a yield greater than 60 to 66 per cent. *under these conditions.*

Knietsch also found that by increasing the period of contact or the quantities of catalytic material the equilibrium was not altered, that is, the yield was not improved. There is, on the other hand, an advantage in removing the SO_3 as quickly as it is formed, as may be foreseen by the law of mass action.

The greatest obstacle encountered by Knietsch, in passing from laboratory experiments to industrial manufacture, was the extraordinary and surprising difficulty in eliminating the last traces of arsenic from the burner gases; this arsenic acted as a poison on the platinum, rendering it inactive. It was possible to obtain the burner gases completely pure only by cooling them slowly in iron tubes and washing them thoroughly with water and with sulphuric acid. In order to ascertain whether the purification was complete the gases were observed optically through a glass tube some metres long. When they were quite pure they appeared transparent and free from mist. The chemical test was made with Marsh's apparatus (*see* Arsenic) on water through which the gas was passed for twenty-four hours. In certain cases great difficulty was found in eliminating a very fine mist formed of finely divided sulphur which could not be separated even by washing the gas repeatedly, so that the catalytic platinum finally became inactive. It was found that these minimal quantities of sulphur were harmful only on account of small traces of arsenic which they contained. This sulphur mist was successfully separated by mixing the burner gases with a little steam.

A difficulty of another kind consisted in the excessive heating of the catalytic substance due to the heat of reaction:

$$SO_2 + O = SO_3 + 86 \text{ Kj. } (20{,}600 \text{ cals.}).$$

Knietsch showed that, contrary to the general opinion up to that time, the yield and the velocity of reaction increase if the tubes containing the platinised asbestos are regularly and continuously cooled.

If the temperature is always maintained by suitable means at about 380° to 450° a yield of 98 per cent. of SO_3 is obtained, and the apparatus works at its maximum capacity. The process is controlled practically by simply watching the temperature of the gases entering and leaving the apparatus.

It was found later that platinum could be economised by replacing the asbestos by other substances which were more porous, for example, the oxides of iron, copper, and chromium, the catalytic action of these substances being then utilised together with that of the platinum.[1]

---

[1] 145 parts of burnt pyrites free from arsenic, in well-sifted pieces of the size of peas, may be taken. This is soaked in 30 parts of a solution of platinum chloride containing 17 grms. of platinum per litre and are then dried at 70°. The platinum is thus finely subdivided and ready for use as a catalyst. This mass does not get crushed together in the apparatus as happens with platinised asbestos, and is very economical. Platinised asbestos is prepared by soaking finely divided asbestos in an aqueous solution of platinum chloride and then in one of ammonium chloride; when the mass is heated to redness the precipitated ammonium platinichloride

The section shown in Fig. 121 gives an idea of the way in which this process has been applied. The well-washed gases from the pyrites burners enter the peripheral part of the apparatus through many openings, *a*, and by passing through the horizontal tubes, *B*, are distributed homogeneously in the flues, *S*, which are interrupted by walls, *C*, in order to force the gas to pass round the tubes containing the catalytic mass. In this way previously cooled gas is used as a cooler for the catalytic mass which is present in the tubes, *R*, and which is heated by the heat developed by the reaction. In order to regulate the temperature of the gases a certain portion of them is passed through the preheater, *G*, before passing through the openings, *a*, whilst another part of the cold gases enters the apparatus directly through the tube *J*. If much gas is passed through *G* the temperature which is established is higher than when a smaller portion passes through it, if the heating surface remains constant; thus the mean temperature of the mixture may be varied at will, and the tubes containing the catalytic mass may be cooled to a greater or less extent. The gases from the various tubes reunite at the top of the apparatus in the tube *F*, and are mixed homogeneously by entering the chamber, *N*, and pursuing a zigzag path before arriving at the tubes *R* containing the catalytic material.

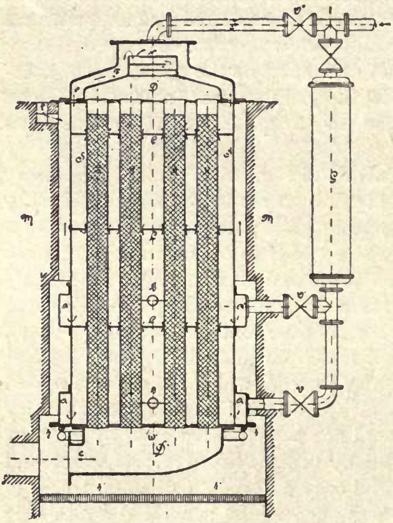


FIG. 121.

In the compartments *D* and *D′* thermometers are placed. The apparatus works well when there is a temperature of 380° in *D* and 450° in *D′*. Under these conditions 96 to 98 per cent. of the SO_2 is transformed into SO_3 with a production of 40 to 50 kilos of SO_3 per tube in twenty-four hours. One kilo of platinum yields one ton of H_2SO_4 per twenty-four hours.

By decreasing the rate of production slightly the yield may be increased to 99 per cent. and may be controlled by analysing the gases in *D′*. At the beginning of the operation the lower compartment of the apparatus is heated by the tube *h* (by means of water gas), and the hot gases escape at the top through the side tube *L*. When the temperature has reached 300° the process continues alone without further heating.

The complete absorption of the SO_3 also presented unforeseen difficulties. It had been noted that, when 1 kilo of SO_3 is dissolved in much water, the heat development is 2090 Kj. (= 499·5 Cals.); on dissolution in much concentrated sulphuric acid at 66° Bé. 1250 Kj. were developed; it therefore appeared easy to absorb all the SO_3 with dilute sulphuric acid from the lead chamber. In actual practice, however, complete absorption was not obtained either with dilute acid or with water. A fog of SO_3 always remained, causing loss and also annoyance to the workmen. After many experiments Knietsch found that the absorption is complete only when concentrated sulphuric acid of 97 to 99 per cent. is employed.

This acid has special properties, which were noted some pages back. Thus its density is at a maximum (more concentrated acid being less dense) and it has also a minimal vapour pressure. With more dilute acid a greater vapour pressure is obtained, due to vapours of H_2SO_4; with more concentrated acid there is also a larger vapour pressure, due to vapour of SO_3, and since the vapours of H_2SO_4 are dissociated into H_2O and SO_3 the minimal *partial pressure* of SO_3 is only obtained with H_2SO_4 of 97 to 99 per cent., and this acid alone is capable of absorbing the SO_3 completely. The concentration of the acid

---

separates platinum in a spongy form. This, however, does not adhere very well to the asbestos and it is now considered better to soak the asbestos or other substance directly in an alcoholic solution of platinum chloride. When the alcohol is burnt away the finely divided platinum, which is very active, alone remains; this catalytic mass contains only 2 per cent. of platinum (Mayert, Ger. Pat. 134,928 of 1901). A more active platinised asbestos, containing 7 to 8 per cent. platinum, is obtained by soaking well-comminuted (but strong-fibred) asbestos in a concentrated aqueous solution of platinum chloride mixed with sodium formate solution and then pressing and drying it.

is maintained constant at about 98 per cent. even during absorption, several absorption vessels being arranged in series so that the SO_3 escaping the vessel charged with the more concentrated oleum passes into others containing 98 per cent. acid, which is supplied continually and passes to successive vessels as it gradually becomes enriched in SO_3. In the Tentelew process (*see later*) use is made of a rational tower of enamelled cast-iron similar to columns for rectifying alcohol; sulphuric acid of any concentration can be fed in at the top of the tower and oleum containing even 25 to 26 per cent. of free SO_3 drawn off from the bottom, where also the SO_3 enters.

By the Badische Anilin und Sodafabrik's process 1 ton of sulphuric acid was obtained per twenty-four hours per kilo of finely divided platinum; to-day even less platinum is employed, and by the Tentelew process 1½ tons of oleum are obtained per kilo of platinum, the absorption tower being fed with 93 per cent. sulphuric acid.

The first German patent of the Badische Anilin und Sodafabrik is dated June 3, 1898 (Ger. Pat. 113,933), and one of the last March 24, 1901 (Ger. Pat. 140,353).

The Farbwerke Meister Lucius und Brüning of Höchst also achieved the catalytic preparation of SO_3 through the discovery of Krauss and Müller von Berneck. The first German patent is that of January 6, 1898 (Ger. Pat. 105,876), and the last one that of February 6, 1902 (No. 135,887). They encountered the same difficulties as the Badische Company and solved them in almost the same way. The heat of reaction between the SO_2 and O was utilised to heat the gaseous mixture of SO_2 and air, furnished by the pyrites burners and cooled by washing with water and with concentrated sulphuric acid.

The arrangement of the apparatus is illustrated in Fig. 122. The cold gaseous mixture enters at *E*, is heated to the desired temperature by passing over the battery of very hot tubes, *R*, and then escapes laterally to descend again through *C* over the catalytic mass and be heated by the reaction which occurs. It then escapes through the tubes *R* and gives up a portion of its heat in order to preheat gases which arrive through *E*, finally passing out at *A*.[1]

The Farbwerke found that they were not tied to the most favourable temperature, but that they could also work at higher temperatures by modifying the equilibrium in a sense favourable to the separation of SO_3 as fast as it was formed, and then passing the gases which had not reacted over the mass a second time. In this way they obtained a yield of 95 per cent. of SO_3 in practice.

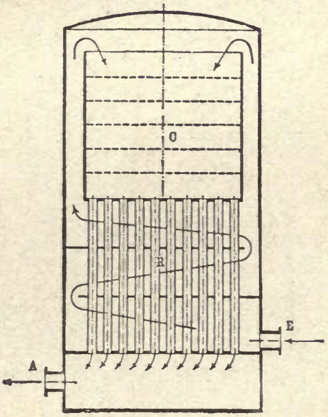


FIG. 122.

The following substances were found to be dangerous to the platinum, as they act as catalytic poisons: As, Se, Te, and Sb. If, however, arsenic is deposited on the contact platinum it can be completely eliminated and the activity of the platinum revived, without removing the latter from the apparatus, by adding a small amount of steam to the gases which pass over the contact mass, while this is heated until the arsenic is expelled. On employing iron oxide, Fe_2O_3, as a catalytic substance, the Farbwerke made the following surprising discovery: if a current of SO_2 obtained from ordinary pyrites burners is passed through a tube containing burnt pyrites at 300° to 400°, less SO_2 is found at the far end of this tube, but the corresponding quantity of SO_3 is *not* present. A part of the SO_2 is thus absorbed by the burnt pyrites, or, more precisely, by the ferrous compounds which this contains. In fact, on adding ferrous sulphate to the burnt pyrites the absorption of SO_2 increases, and becomes complete and quantitative if the gases contain a small amount of moisture. When the burnt pyrites is now heated to 550° in presence of SO_2, all the SO_2 which has been previously absorbed is liberated in the form of SO_3 and H_2SO_4.[2]

---

[1] The steam necessary for driving the pump which keeps these large masses of gas in circulation was obtained from the hot gases from the pyrites burners, which, at a temperature of 500° to 600°, pass over iron tubes in which water from special boilers circulates.

[2] The Farbwerke found that the following substances also acted as catalysts: vanadic acid, tungstic acid, molybdic acid, and their mutual combinations; also the more highly oxidised oxides and sulphates of Fe, Co, Ni, Cu, Ag, Mn, Cr, and U, etc., and also the oxides of Ce, Dy, La, Zr, Th, Ti, Si, and those of certain other rare elements. Finely divided platinum is the most energetic

The catalytic reaction of the burnt pyrites becomes greater when ferrous sulphate is present, because this is first oxidised and then decomposed, forming finely divided iron oxide, Fe_2O_3, which is then much more active. The residual sulphur, which is ordinarily contained in burnt pyrites, is then also utilised and transformed into SO_3, the burnt pyrites becoming redder. A new process of preparation of SO_3 and of H_2SO_4 has been evolved from these experiments and is illustrated schematically in Fig. 123. The burnt pyrites soaked in ferrous sulphate solution—which is obtained during the treatment of burnt pyrites containing copper (*see* Copper Sulphate)—is raised by means of an elevator, *L*, and then continuously passed into a tube, *C*, by means of a screw conveyor, *E*. The rotating tube, *C*, is made of wrought-iron, and the contents are well distributed by means of fixed longitudinal plates throughout its length (*see* section to left of figure). The tube is rotated on the carrier, *H*, by means of the cog-wheel, *F*; the burnt pyrites descends the tube in the opposite direction to the current of hot gases which passes in from the pyrites burners, *A*. In the upper and colder part of the tube all the SO_2 is absorbed by the burnt pyrites, and this gradually descends into the lower hotter part of the tube where all the S and SO_2 are completely liberated in the form of vapours of SO_3 and H_2SO_4. These vapours travel up the tube and enter the chamber K_2, together with the indifferent gases of the atmosphere. In this chamber the dust carried over with the gases is deposited, the gases then passing through the tube *S* into the absorbing or condensing apparatus. The burnt pyrites, free from sulphur, is collected in the chamber K_1, and may then be continually re-employed in order to utilise all the sulphur which it contains (1 to 2 per cent.) in the state of sulphide.

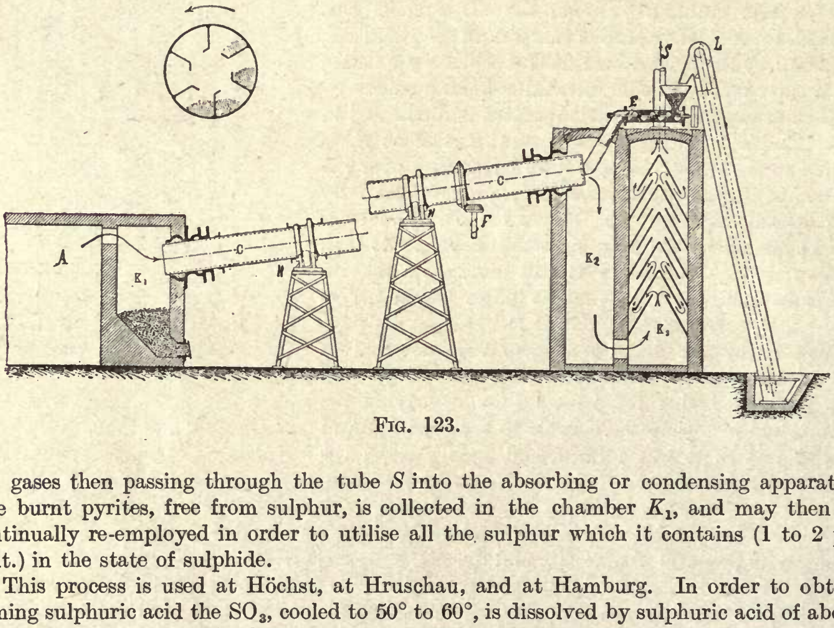


FIG. 123.

This process is used at Höchst, at Hruschau, and at Hamburg. In order to obtain fuming sulphuric acid the SO_3, cooled to 50° to 60°, is dissolved by sulphuric acid of about 95 per cent. strength. To obtain ordinary sulphuric acid the gases are dissolved in water or dilute sulphuric acid. If a concentration of more than 95 per cent. of H_2SO_4 is reached, the acid, which was at first clear, becomes opalescent, because a little ferrous sulphate which is formed in the apparatus and which is soluble only in acid of less strength than 95 per cent., is separated. If the acid is turbid it is readily and completely cleared by adding a little water.

In the Schröder-Grillo process a very active catalytic substance is used which is

---

of all these substances, and under certain conditions produces a very energetic catalytic reaction even at 200° (instead of 450°).

Russell and Smith showed in 1901 that the following oxides and hydroxides: MnO_2, PbO_2, Fe_2O_3, and Cr_2O_3, also act catalytically on $SO_2 + O$, even in the cold, in proportion to the contact surface, but all action ceases if these substances are perfectly dry. Even with hot platinum the reaction is minimal or zero if the substances are absolutely dry, whilst it is greatly accelerated by a mere trace of steam. On the other hand, an excess of steam acts as a poison on the platinum and the catalytic action is reduced to a minimum. The mixture of dry gases as it is now prepared industrially, even after drying with strong sulphuric acid, always contains traces of moisture which are highly favourable to the catalytic action.

obtained by subdividing platinum in a magnesium salt; magnesium sulphate is soaked in a solution of a platinum salt and then heated in presence of SO_2, when finely divided platinum separates.

This catalytic mass is very economical because it is very dilute, and contains only one one-hundredth part of the platinum contained in platinised asbestos;[1] with 500 mgrms. of finely divided platinum one ton of oleum is produced per day with a consumption or loss of only 20 mgrms. of platinum per ton of acid. The brown coloration often found in acid obtained by this process is removed by the addition of lead peroxide followed by filtration through sand.

About thirty works employ this process to-day and the yields are from 96 to 98 per cent. The first patent obtained was that of Schröder-Grillo of Hamborn of May 17, 1898 (Ger. Pat. 102,244), and the last that of May 20, 1901, which is an English patent.

The process of the Verein chemischer Fabriken in Mannheim was discovered by A. Clemm and Hasenbach. The first patent obtained was that of July 31, 1898 (Ger. Pat. 107,995), and the last that of December 31, 1901, which is an American patent. The process is based on the observation made by Lunge in 1878, that when gases from the pyrites burners are passed over red-hot burnt pyrites, Fe_2O_3, 18 per cent. of the SO_2 contained in the gases is converted into SO_3.[2]

By the new process the pyrites is burned in previously dried air in such a manner that gases containing 2 to 3 per cent. of SO_2 are obtained. The burners are completely encased in sheet iron and thus hermetically closed in order to prevent the entrance of moist air. The purified gases enter the first chamber, which contains a layer of 2 to 3 metres of burnt pyrites (ferric oxide, Fe_2O_3) which at a temperature of about 600° transforms 60 per cent. of the SO_2 into SO_3. The SO_3 is then all absorbed by means of sulphuric acid, and the remaining SO_2, which is dry and pure, enters another compartment where it comes into contact with finely divided platinum and is then completely transformed into SO_3.

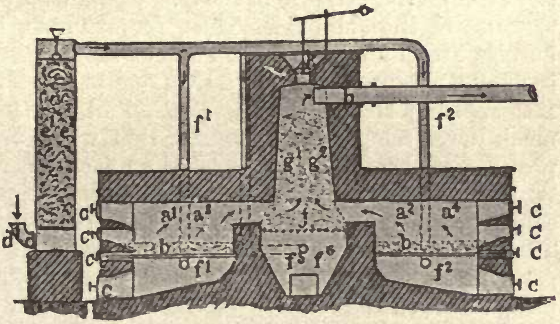


FIG. 124.

Fig. 124 illustrates diagrammatically two compartments of the pyrites burner where the combustion of the ore, a^1, a^2, a^3, a^4, takes place.

The air needed for the combustion passes in through the tube *d*, through a drying tower, e^1, e^2, and then through the tubes f^1, f^2, below the grate of the furnace.

The mixture of SO_2 and air enters a tall chamber, g^1 and g^2, containing the catalytic mass of burnt pyrites which transforms the SO_2 into SO_3 at a definite temperature. If necessary a larger quantity of air may be passed in directly through the tube f^5. The SO_3 which is formed passes out through the tube *b* to the condensing apparatus; the unaltered SO_2 is passed over the platinum contact mass. In order to renew the iron oxide this is discharged through the revolving grate, *j*, and the chamber is then recharged with new burnt pyrites through the upper opening, *K*.

In his theoretical explanation of catalytic phenomena Lunge maintains that the increase of the velocity of reaction which is considered by Ostwald as a simple manifestation of catalytic action may be explained in these cases by the formation of intermediate products; in the case of platinum we may suppose these to consist of easily decomposable intermediate oxides. As a

---

[1] *See also* Notes on pp. 321, 323. Schröder found that the catalytic mass is damaged by silicon fluoride, which is often present in burner gases; it is therefore advisable to separate this before the gases pass over the platinum. Arsenic deposited on the platinum is removed by *aqua regia* or chlorine.

[2] It was also found that chromium and manganese oxides and the corresponding sulphates increase the activity of iron oxide. In 1902 Lunge and Pollitt found that copper and arsenic oxides also have a beneficial effect on the catalytic activity of iron oxide.

matter of fact Wöhler discovered oxides of platinum in 1909. The supposed catalytic action of iron oxide may be explained experimentally by the intermediate formation of ferric sulphate which has a temperature of decomposition very close to that of its formation, and we can understand how under certain conditions SO_3 continues to be formed by decomposition of the sulphate, so that apparently unaltered iron oxide finally results:

$$Fe_2O_3 + 3SO_2 + 3O = Fe_2(SO_4)_3:$$

and this then decomposes as follows: $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$.

In 1902 Keppeler observed, indeed, that iron oxide first forms ferric sulphate which, at a temperature of 400°, commences to liberate molecules of SO_3, until the partial pressure of this gas (*see* p. 74) is equal to the decomposition pressure of the ferric sulphate. The decomposition pressure of the sulphate varies with the temperature and depends on the vapour pressure of SO_3. Towards 600° complete dissociation of the sulphate takes place at the ordinary pressure (1 atmosphere), that is, at that temperature the dissociation pressure of the sulphate has overcome the partial pressure of the SO_3. Decomposition may, however, occur also at lower temperatures, because at these temperatures the partial pressure of the SO_3 vapours may be lower than the dissociation pressure of the sulphate. Thus, for example, if the gases from the pyrites burners are diluted to such an extent that a gas containing 8 per cent. of SO_3 is finally obtained, the partial vapour pressure of the SO_3 will be $\frac{8}{100}$ of an atmosphere. Hence, the dissociation of the ferric sulphate will occur at a much lower temperature, namely, that which corresponds with a dissociation pressure of the sulphate of $\frac{8}{100}$ of an atmosphere.

Keppeler has observed that the dissociation pressure of the sulphate always commences at about 500°, whilst its temperature of formation is a little lower. Thus, on working with an excess of oxygen, that is, with very dilute burner gases (2 to 3 per cent. of SO_2), this temperature suffices for the continuous formation and dissociation of the sulphate. If the oxygen is not present in excess, then, according to the law of mass action, the temperature of formation of the sulphate will be higher. If abundant quantities of this gas are present, that is, if there is great dilution with air, the heat of reaction will raise the temperature of the entire catalytic mass only slightly, and thus the disadvantageous dissociation of SO_3 in contact with the very hot catalytic mass will be diminished (*see above*).

Since burnt pyrites produces its maximum catalytic effect at 625° and since at that temperature a portion of the SO_3 is already dissociated, we can understand why the highest yield which can be obtained by this method is only 70 per cent. and why the remaining SO_2 has therefore to be transformed by means of a platinum catalyst.

L. Heinz (U.S. Pat. 875,909 of 1908) has proposed the purification of the gases which are to be brought into contact with the catalytic mass by first transforming about 20 per cent. of the SO_2 into sulphuric acid in a system similar to that of the lead chambers and then passing the remaining gases, freed from arsenic and from fog, over the catalytic mass.

Since 1911 considerable use has been made throughout Europe of oleum plants on the Tentelew system (Ger. Pat. 227,095, 1909), which is an improvement on the process of the Badische Anilin und Sodafabrik, owing to enhanced purification of the gas by means of a special dust chamber formed of a large number of perforated iron sheets, to the rational and intense cooling of the gas and its filtration, washing, and drying in towers by means of sulphuric acid, and especially to the ingenious enamelled absorption towers in which the SO_2 is fixed by sulphuric acid. In the Tentelew process the contact material consists of special asbestos containing up to 8 per cent. of platinum. The heat of the catalytic reaction is efficiently recovered, so that no fuel is consumed, whereas with the Grillo-Schröder system 10 to 12 kilos of fuel are consumed per 100 kilos of acid. The Tentelew process transforms 98 per cent. of the SO_2 into SO_3 and gives oleum as clear as water.

The gas is circulated by means of a powerful turbo-fan, which draws the gases from the burners to the drying towers and then forces them through the catalytic apparatus and the absorption towers.

Units have been constructed for producing 5000 tons of oleum per annum, each unit requiring more than 150 tons of lead plant and about 9 kilos of platinum as platinised asbestos. In 1917 there were ten units at work in the Cengio works of the Società Italiana Prodotti Esplodenti and two at Vicenza belonging to the Union of Fertiliser Manufacturers, while another unit is to be erected at Bovisa (Milan).

The process of Rabe (1901) deserves to be recorded; it is distinguished by various improvements in the details of certain operations. In this process there is a special arrangement for purifying and drying the gases from the pyrites burners, by means of which even traces of HCl are removed with sodium bisulphate crystals. By cooling the concentrated sulphuric acid which absorbs the SO_3, by suitable means, a very concentrated oleum may be obtained. Several works use Rabe's process; in one of these the complete cost of one ton of SO_3, which includes all expenses, sinking fund, etc., is about £2.

Finally we may mention the process of Hölbling and Ditz (Ger. Pat. 149,677 of 1903), in which a mixture of the sulphates of thorium and cerium is used as a catalyst, together with a little praseodymium sulphate, which raises the yield to 92 per cent. Küster obtains good results by employing vanadium pentoxide at 450° as a catalyst, and suitably regulating the amount of moisture.

According to Ger. Pat. 280,960 (Farbenfabriken vorm. Fried. Bayer, 1912) asbestos with 20 per cent. of silver vanadate has a catalytic effect greater than that of silver or vanadium and is able to transform SO_2 quantitatively into SO_3.

Vessels for preparing and storing fuming sulphuric acid must not be made of cast-iron, although this resists ordinary sulphuric acid monohydrate so well, as these are easily broken and even exploded by oleum, which penetrates into the pores of the metal, producing H_2S, SO_2, and CO (the latter being formed from the carbon in the cast-iron). Wrought-iron receivers are slightly corroded by weakly fuming acid (up to 27 per cent. of free SO_3), perhaps because such oleum has a greater electrical conductivity than acid of other concentrations. If the oleum contains more than 27 per cent. of free SO_3, wrought-iron vessels resist its action very well, and remain unaltered for years. Acid thus stored is free from iron (less than 0·008 per cent.), and such acid is in request for use in accumulators and in the manufacture of pure aluminium sulphate. Vessels of enamelled cast iron are more resistant.

For the construction of all catalytic plants various materials are used. The gases from the pyrites burners are very hot (above 200°), and until they leave the dust chamber they circulate in cast- or wrought-iron pipes, either naked or with an internal coating of refractory material. When the gases leave the cooler (of lead), and are cold but moist, they pass through lead pipes, the filters and the adjacent columns being wholly of lead. For the cold, dry gases, tubes and vessels of wrought-iron or steel are used. Gases containing hot gaseous sulphur trioxide are passed through wrought-iron tubes. The absorption towers, into which these gases pass when cold, are of enamelled cast-iron or of cast steel.

The cost of production in Germany, according to Luty and Niedenführ, is as follows: one ton of sulphuric acid calculated as monohydrate obtained in lead chambers at 50° Bé. or by catalytic methods from sulphur trioxide, and in a plant with a daily production of twenty tons of monohydrate will cost as follows (p. 328).

Under these conditions it is obvious that the last hour of the lead chambers is not very remote, and although these may continue to be used for some time, this is due to the fact that during the last few years, under the stimulus of the new competing process, numerous and important improvements in the lead chamber process (as recorded above) have been introduced. The catalytic process is, however, also being continually improved, and the patent licences continually cost less and less and in a few years will be public property. Certain technical experts have testified that supervision and regulation are easier with the catalytic process than with lead chambers.

	Old plant with lead chambers and burners worked by hand	New plant with two lead chambers, five plate-towers, and mechanical burners.	Catalytic process under the best modern conditions
	Shillings	Shillings	Shillings
Pyrites	12·80	12·80	12·80
Nitrate	2·08	2·08	—
Fuel for heating and power	1·92	1·92	1·60
Labour	2·24	1·68	1·92
Repairs	1·36	1·20	1·20
Sinking fund and interest:			
(*a*) Plant and land	5·04	3·68	6·72
(*b*) Patent expenses (£4000) . .	—	—	1·04
Cost of dilution of the catalytic sulphuric acid . . . . . . about	—	—	1·60
Cost of one ton monohydrate without general expenses	25·44 = (£1 5*s.* 5*d.*)	23·36 = (£1 3*s.* 4½*d.*)	26·88 = (£1 6*s.* 10½*d.*)

To-day already the advantage of the catalytic process is very great when sulphuric acid monohydrate or even concentrated acid of 66° Bé. is to be prepared, because on distilling in platinum apparatus this acid costs at least £1 12*s.* per ton, whilst catalytically it costs about £1 7*s.*

For large plants the Badische process or, better, that of Tentelew, appears to be the most convenient and for small plants the process of Rabe or of Schröder-Grillo.

DERIVATIVES OF SULPHURIC ACID

PERSULPHURIC ACID, $H_2S_2O_8$ or HSO_4. This acid is not known in the free state, but is formed when sulphur heptoxide, S_2O_7, is dissolved in water. The latter compound is obtained in a crystalline, easily fusible, and easily alterable condition by passing an electric discharge through a mixture of oxygen and SO_2. It is also formed in electric accumulators. A solution of persulphuric acid is easily obtained with the apparatus of Elbs and Schönherr (Fig. 125). Sulphuric acid of sp. gr. 1·4 is placed in the test-tube, *A*, and a current of 2 amps. and a density of 100 amps. per square decimetre of electrode surface is passed between the platinum anodes and cathodes by means of the arrangement indicated in the figure. Ice and water are placed in the vessel, *F*, in order to cool the apparatus, and the gases formed at the anode during electrolysis escape through the tube *E*. M. G. Levi (1903) and Blumer (1911) showed that better yields (calculated on the current) are obtainable if a temperature of 30° is not exceeded; under other conditions the Caro's acid (*see below*) formed during the electrolysis acts as a depolariser and lowers the yield. E. Müller (1912) found that the concentration of the persulphuric acid increases with increase of the current concentration (*i. e.*, the ratio between the current intensity and the volume of the electrolyte). Müller and Schellhaus (1907) showed that the Caro's acid may be decomposed as it is formed and the anodic polarisation raised by addition of small quantities of sulphites, or of hydrochloric or chloric acid. The addition of ferricyanide

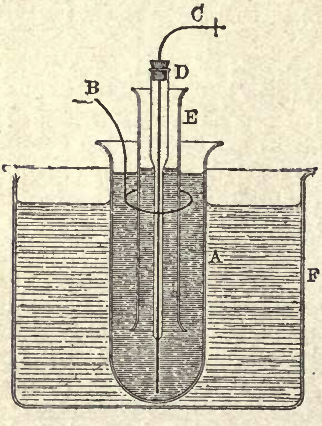
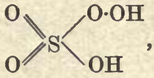
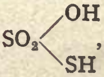


FIG. 125.

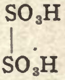
is also advantageous (Blumer, Ger. Pat. 205,067, 1912); C. Scholl and Andrich (1912) used potassium bisulphate and ferricyanide. According to Ger. Pats. 172,508 and 205,069, persulphates may be obtained by electrolysis of sodium or potassium bisulphate. The solution is decomposed on heating, forming H_2SO_4, nascent oxygen and ozone. The solutions decolorise indigo, but not permanganate solutions, and they produce no blue coloration with solutions of bichromates, this acid being thus distinguished from hydrogen peroxide.

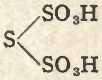
The persulphates and their applications are dealt with in Part III.

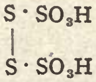
CARO'S ACID (Oxypersulphuric acid), H_2SO_5. The formula HSO_5 or $H_2S_2O_9$ was first attributed to this acid, and its constitution, , was established by a series of investigations extending from 1898 to 1910 (Baeyer and Villiger, D'Anse and Friedrich). Caro obtained it (1898) by dissolving ammonium or potassium persulphate, with shaking, in concentrated sulphuric acid and cooling the solution in ice. The resulting mass, at first pasty and then solid, has considerable oxidising power and under the name of Caro's reagent is used in investigations on the alkaloids. In the free state it is known only in solution, and its salts are unknown. According to Ger. Pat. 105,857 (1898) and the supplementary Pat. 110,249, Caro's acid may be obtained by electrolysing and cooling concentrated sulphuric acid (sp. gr. 1·5) until the persulphuric acid first formed disappears; if dilute, hot sulphuric acid is used, Caro's acid is not formed: $Na_2S_2O_8 + H_2O = Na_2SO_4 + H_2SO_4 + O$. It is used for oxidising aromatic monamines, first to the nitroso- and then to the nitro-derivative (*see* Vol. II., "Organic Chemistry"); aniline is thus converted directly into nitrobenzene. It readily liberates iodine from potassium iodide solution and can thus be determined easily by titration.

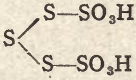
THIOSULPHURIC ACID, , is not known in the free state, and when liberated from its salts (thiosulphates) by means of strong acids it decomposes at once into $SO_2 + S + H_2O$. The salts are obtained by heating sulphites with sulphur: $SO_3Na_2 + S = S_2O_3Na_2$, or by heating sodium sulphide and sodium sulphite with iodine.

POLYTHIONIC ACIDS: these all contain six atoms of oxygen and two of hydrogen, with varying numbers of atoms of sulphur. They may also be considered as condensation products of two sulphonic acid groups by means of sulphur atoms.

DITHIONIC ACID:  $\begin{array}{c}SO_3H\\ |\\ SO_3H\end{array} = S_2O_6H_2$. This is known only in solution and is obtained from manganous dithionate, MnS_2O_6. When heated, it forms $SO_2 + H_2SO_4$.

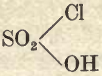
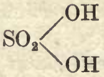
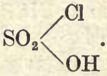
TRITHIONIC ACID:  $= S_3O_6H_2$, is not known in the free state; the potassium salt is obtained either by heating acid potassium sulphite in aqueous solution with flowers of sulphur, or from sulphites with thiosulphates and iodine. With strong acids it gives S and SO_2.

TETRATHIONIC ACID:  $\begin{array}{c}S\cdot SO_3H\\ |\\ S\cdot SO_3H\end{array} = S_4O_6H_2$. The salts of this acid are obtained from thiosulphates with iodine: $2S_2O_3K_2 + I_2 = S_4O_6K_2 + 2KI$.

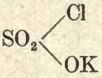
PENTATHIONIC ACID:  $= S_5O_6H_2$, is obtained together with tetrathionic acid by passing H_2S into an aqueous solution of SO_2 at 0°: $5SO_2 + 5H_2S = H_2S_5O_6 + 4H_2O + 5S$, by which means *Wackenröder's liquid* is formed.

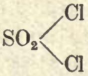
In contradistinction to sulphuric acid all the polythionic acids yield highly soluble barium salts.

CHLORO-ANHYDRIDES OF SULPHURIC ACID. These may be considered as sulphuric acid in which one or both of the OH groups are replaced by chlorine. They are obtained by treating sulphuric acid with phosphorus pentachloride (PCl_5); these anhydrides regenerate sulphuric acid with water.

The **monochloro-anhydride** of sulphuric acid,  $SO_2<\begin{matrix}Cl\\OH\end{matrix}$, is also called **chloro-sulphonic acid,** and is formed by the following reaction:  $SO_2<\begin{matrix}OH\\OH\end{matrix}$ $+ PCl_5 =$ $HCl + POCl_3 +$  $SO_2<\begin{matrix}Cl\\OH\end{matrix}$. The phosphorus oxychloride, $POCl_3$, which is thus formed, reacts further with sulphuric acid, generating more chloro-anhydride and metaphosphoric acid. It is also obtained from SO_3 or pyrosulphuric acid ($H_2S_2O_7$) by treatment with HCl vapour. It is prepared still more conveniently by passing chlorine through cooled sulphuric acid into which phosphorus trichloride is slowly dropped.

According to the Saccharin-Fabrik vorm. Fahlberg (Ger. Pat. 228,424, Sept. 1909), gaseous hydrogen chloride is passed continuously into a solution of sulphur trioxide in chlorhydrin; this solution can be cooled without separation of solid sulphur trioxide. In this way distillation of the chlorhydrin is avoided.

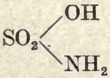
It is a colourless, fuming liquid of sp. gr. 1·776 at 18°, and boils without change at 153°. When heated above 153° it dissociates partially into Cl, SO_2, and H_2SO_4. Its heat of formation from SO_3 and HCl is 14,400 cals., its heat of solution in water 40,300 cals., and its heat of evaporation 12,800 cals. per mol. (116·5 grms.). In moist air or, better, in water it decomposes into HCl and H_2SO_4. When heated with NaCl, it gives HCl and SO_3Cl Na. It is used for various organic syntheses (*e. g.*, that of saccharin, *see* Vol. II., "Organic Chemistry"). Its potassium salt,  $SO_2<\begin{matrix}Cl\\OK\end{matrix}$, is obtained by the action of SO_3 on KCl.

The **dichloro-anhydride** of sulphuric acid  $SO_2<\begin{matrix}Cl\\Cl\end{matrix}$ is also called **sulphuryl chloride,** sulphuryl being the name of the SO_2 group of sulphuric acid. It is easily obtained by direct interaction of Cl and SO_2 in presence of a little camphor, and may be distilled.

It is a colourless liquid of pungent odour which fumes less in the air than the monochloro-anhydride; it has a specific gravity of 1·667 and boils unchanged at 69°.

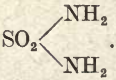
A chloro-anhydride of pyrosulphuric acid, termed **pyrosulphuryl chloride,** $S_2O_5Cl_2$ ($Cl{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}Cl$), is obtained by heating 16 kilos of SO_3 with 21 kilos of PCl_5 in a reflux apparatus and is separated by fractional distillation. It is a colourless, mobile, highly refractive liquid, which fumes in the air; its sp. gr. is 1·819 at 18°, its heat of formation 180,600 cals., and its heat of evaporation 7570 cals. It boils at 142° and it is very hygroscopic, being transformed into chlorosulphonic acid (*see above*) by moist air and slowly into HCl and H_2SO_4 by water. It reacts with organic substances so violently as to char them and at a high temperature it is decomposed into Cl, SO_2, and SO_3. With NaCl it develops much heat and forms a fuming, transparent, solid mass. The chloro-anhydride of sulphurous acid, $SOCl_2$, also called **thionyl chloride,** is likewise known.

AMINO DERIVATES OF H_2SO_4. These compounds have constitutions analogous to those of the chloro-anhydrides, the OH groups of sulphuric acid being replaced by the ammoniacal residue, NH_2 (amino): thus we have:



$SO_2<\begin{matrix}OH\\NH_2\end{matrix}$;

Aminosulphonic acid or sulphaminic acid



$SO_2<\begin{matrix}NH_2\\NH_2\end{matrix}$.

Sulphamide or amide or sulphuric acid

SULPHAMIDE is obtained, mixed with sulphimide, from NH_3 and SO_2Cl_2, and forms large colourless crystals which melt at 81°. It is soluble in water and has a neutral reaction. The hydrogen united to nitrogen is replaceable by metals. When heated to 200° it forms *sulphimide*, SO_2NH, in which two hydrogen atoms of NH_3 are replaced by the sulphuryl residue; the residue NH is called *imino*. The hydrogen atom of the imino group is also replaceable by metals, and salts are thus formed which are better crystallised and more stable than sulphimide itself.

SULPHAMINIC ACID is obtained from SO_3 and dry NH_3.

An iminosulphonic acid, $NH(SO_3H)_2$ (= disulphaminic acid), is known, and also a nitrilesulphuric acid, $(NSO_3H)_3$ (trisulphaminic acid), both containing the monovalent SO_3H group, called the *sulphonic* group.

OXYGEN COMPOUNDS OF Se and Te

SELENIUM DIOXIDE, or SELENIOUS ANHYDRIDE, SeO_2. This compound is formed on burning selenium in oxygen or air. With potassium iodide dissolved in hydrochloric acid, selenium and iodine are separated:

$$SeO_2 + 4KI + 4HCl = 4KCl + 2H_2O + Se + 2I_2.$$

It is a white substance, forming needles which sublime at about 320° without melting. It is easily soluble in water, being transformed into selenious acid, SeO_3H_2. This acid is also obtained by dissolving selenium in concentrated nitric acid and forms large colourless crystals which decompose into $SeO_2 + H_2O$ when heated. Selenious acid is reduced by sulphur dioxide with separation of selenium and formation of sulphuric acid:

$$SeO_3H_2 + 2SO_2 + H_2O = Se + 2SO_4H_2.$$

With H_2S its solutions give a yellow colloidal solution of selenium sulphide, which becomes red under the influence of time, heat, light, or pressure. Its salts are called *selenites.*

SELENIC ACID, SeO_4H_2. This acid is obtained by oxidising selenious acid with chlorine: $SeO_3H_2 + H_2O + Cl_2 = 2HCl + SeO_4H_2$. When pure it forms crystals which melt at 58°; at a concentration of 95 per cent. (sp. gr. 2·6) it forms a dense oily liquid. A hydrate, SeO_4H_2, H_2O, is known, but selenic anhydride is not known. The salts of the acid are called *selenates.*

TELLURIUM DIOXIDE, TeO_2. This substance is obtained as a white crystalline mass by burning tellurium; it melts at a red heat, and then sublimes. It is almost insoluble in water. *Tellurious acid,* H_2TeO_3, is formed on dissolving tellurium in nitric acid, and separates from the solution as a white powder on diluting with water. This powder is decomposed on heating, forming TeO_2 and H_2O.

TELLURIC ACID, H_2TeO_4. This compound is obtained by oxidising tellurious acid with chromic acid. It is separated from the solution as a white powder by means of concentrated nitric acid. It is only slightly soluble in water and has a feebly acid reaction. When heated carefully it decomposes into water and telluric anhydride (TeO_3), which forms a yellow powder insoluble in water.

NITROGEN GROUP

This group is composed of the elements: *nitrogen, phosphorus, arsenic,* and *antimony.*

Together with nitrogen we shall also study the new gases which have recently been discovered in the atmosphere, namely, argon, helium, krypton, xenon, and neon, which are elements fitting well into the periodic system of the elements, but have been little studied so far, as no compounds of them are known. The elements of the nitrogen group follow the same rule as those of the other groups, that is, their melting- and boiling-points rise with increase of the atomic weight, and the matter of which they are composed becomes condensed so that they acquire a more or less metallic aspect at the same time. However, in this group also, the resemblance is more pronounced between arsenic and antimony, whilst there are notable differences between the solid and much more active phosphorus, and gaseous nitrogen, which is more inert. All these elements form hydrogen compounds containing three atoms of H, while other less important hydrogen compounds are also known.

As the molecular weights of the hydrides increase, the basic character diminishes and then disappears. Ammonia, NH_3, has an alkaline reaction and is a strong base, readily forming ammonium salts with acids. Hydrogen phosphide, PH_3, is less basic and at ordinary temperatures combines with only HBr and HI. Hydrogen arsenide, AsH_3, and hydrogen antimonide, SbH_3, are not basic.

The oxygen compounds of nitrogen are strongly acid, whilst those of antimony are quasi-basic. The acid compounds of the halogens, whether oxygenated or not, contain one hydrogen atom in the molecule: HCl, $HClO_3$, $HClO_4$; those of the sulphur group contain two atoms of hydrogen: H_2S, H_2SO_3, H_2SO_4, etc. (similarly for selenium and tellurium); those of the nitrogen group usually have three hydrogen atoms: NH_3, PH_3, AsH_3, SbH_3, H_3PO_4, H_3AsO_4, H_3AsO_3, etc.

These acids with three atoms of hydrogen are called ortho-acids or normal acids, and if 1 mol. H_2O is deducted from them they are converted into the so-called meta-acids, containing only one atom of hydrogen: metaphosphoric acid, HPO_3 (*i. e.*, $H_3PO_4 - H_2O$); sodium meta-arsenite, $NaAsO_2$ ($= Na_3AsO_3 - Na_2O$).

For nitrogen only the meta-acids, and not the ortho-acids, are known. Thus, ordinary nitric acid, HNO_3, corresponds with the hypothetical orthonitric acid, H_3NO_4, and ordinary nitrous acid, HNO_2, with the hypothetical orthonitrous acid, H_3NO_3.

NITROGEN: N, 14.05

[IN FRENCH AZOTE, OFTEN WRITTEN Az]

Rutherford in 1772 by his studies on respiration, and Priestley simultaneously by burning substances in a closed bell-jar, showed that when the oxygen of the air is exhausted a constant volume of inert gas remains, mixed with the carbon dioxide formed by combustion and respiration. They called this gas *mephitic* or *phlogisticated air*.

In 1777 Scheele showed that air is composed of two gases, oxygen and nitrogen.

Nitrogen is found free in nature in the atmosphere, of which it forms about four-fifths (by volume). It is also found in abundance combined in the form of ammonium salts and nitrates, and is an essential and characteristic constituent of the organic substances of the animal kingdom, such as albuminoids, blood, muscles, and nerves. It is found less abundantly in the vegetable kingdom, in seeds, etc., in the form of albuminoids, amino-acids, etc.

PROPERTIES. Nitrogen is a colourless, odourless gas: 1 litre weighs 1·2507 grms., and it has a specific gravity compared with air of 0·97. Its critical temperature is − 146° and its critical pressure 35 atmospheres. In the liquid state it is colourless, boils at − 194° at a pressure of 1 atmosphere, has a specific gravity of 0·804 (water = 1), and solidifies at − 214°. At − 252° it has the specific gravity 1·0265, whilst that of solid oxygen at the same temperature is 1·4256 (Dewar, 1904). One litre of water at 10° dissolves 16·1 c.c. of gaseous nitrogen. The heat of evaporation of liquid nitrogen at − 183° is 48 cals., that of oxygen at − 185° being 51 cals.

The heat of dissociation absorbed by each diatomic gram-molecule during the liberation of the two atoms is 13,020 cals., the value for oxygen being 26,320 cals.

Nitrogen was formerly believed to be a chemically indifferent gas, incapable of combining directly with any other substance. To-day, however, the conditions have been found for obtaining compounds of nitrogen directly, and these are very numerous and important. Lithium, for example, burns in an atmosphere of nitrogen at high temperatures, and so do magnesium, boron, and silicon, forming *nitrides:* $3Mg + N_2 = Mg_3N_2$. Nitrogen combines directly with many metallic carbides (*see below*) and with various other substances under the action of electricity or of organic or inorganic catalysts. If an electric spark is passed through a mixture of nitrogen and oxygen, or of nitrogen and hydrogen, a chemical reaction occurs, and in the first case nitrogen trioxide, N_2O_3, and in the second ammonia is formed. In the atmosphere, in which nitrogen, oxygen, and water are present, electric discharges produce ammonium nitrite and nitrate.

In 1893 Threlfall found that discharges between an electrode of mercury and another electrode in an atmosphere of nitrogen lead to the formation of an explosive nitride. This observation was confirmed by Strutt for active nitrogen and in 1914 J. Kowalski showed that, if a flask containing nitrogen free from oxygen is partially surrounded by copper conductors between which a high tension current is passed, luminous phenomena and maybe explosion occur in the flask, owing undoubtedly to the formation of active nitrogen.

By means of the electric discharge Strutt also obtained an allotropic form of nitrogen, which is luminous in the dark and is able to transform yellow phosphorus into the red variety.

Nitrogen does not support combustion, still less the vitality of organisms, because it plays no part in respiration, although it is not poisonous. In an atmosphere of nitrogen animals slowly die, the oxygen in their lungs which is necessary in order to transform the blue venous blood into red arterial blood being gradually diminished.

PREPARATION. When a current of air is passed over compounds which absorb oxygen, such as red-hot copper, a hydrochloric acid solution of cuprous chloride, or an alkaline solution of pyrogallol, or when yellow phosphorus is burnt in a bell-jar containing moist air, all the oxygen is absorbed in the form of solid or liquid compounds, and free nitrogen remains. Until the year 1894 it was believed that the nitrogen obtained in this way was pure, but the numerous experiments of Ramsay and Rayleigh showed that it is a mixture of nitrogen with about 1 per cent. of argon. Other new elementary gases, previously quite unknown, were found later in the atmosphere. In practice nitrogen may be prepared conveniently from a mixture of 1 part of sodium nitrite, 1 to 2 parts of ammonium sulphate, and 1 part of normal potassium chromate or a few drops of ammonia (to fix the acids which may be formed), together with 5 parts of water. The whole is heated in a glass retort and the nitrogen developed is purified by passing it through dilute sulphuric acid, which retains the ammonia, whilst traces of oxygen are absorbed by passing it over red-hot copper:

(*a*) $2NO_2Na + SO_4(NH_4)_2 = Na_2SO_4 + 2NO_2NH_4$ (ammonium nitrite).
(*b*) $NO_2NH_4 = 2H_2O + N_2$.

Pure nitrogen is obtained by heating ammonium bichromate or a mixture of potassium bichromate and ammonium chloride in a retort. Another method of obtaining nitrogen consists in passing chlorine into a concentrated solution of ammonia, avoiding an excess of chlorine, which would form a highly explosive substance (nitrogen chloride):

$$2NH_3 + 3Cl_2 = N_2 + 6HCl \text{ (which forms } NH_4Cl \text{ with HCl).}$$

Pure nitrogen is also obtained by acting on urea with nitrous acid:

$$CO(NH_2)_2 \text{ (urea)} + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

The carbon dioxide so formed is easily removed by passing the gas through a solution of sodium hydroxide. Many organic nitrogen compounds (diazo-compounds) also yield nitrogen when simply heated, for example, diazonaphthalenesulphonic acid with alcohol and sulphuric acid. Certain micro-organisms (*Denitrifying bacteria* studied by Wagner

Burri, Stutzer, and Calmette) have the property of transforming organic and nitric nitrogen into free nitrogen, and this is of great importance to agriculture, because these bacteria are nourished more especially by the pentosans contained in straw and destroy the nitrogenous material of stable manure. Calcium nitrate resists this action better than sodium nitrate. Cingolani in 1909 found two bacteria in calves' excrement called *Bact. porticensis denitrificans* (α and β); the β-variety reduces nitrates to nitrites, whereas the α-bacteria do not attack the nitrates, but reduce the nitrites to free nitrogen, and sometimes to ammonia. Similar bacteria were found by Calmette in 1904 in the bacteria beds used in the purification of sewage (*see* p. 249). The denitrifying bacteria almost always form large amounts of nitrous oxide, N_2O, from the nitrates (Beijerinck and Minkmann, 1909). In 1897 Sewerin described a *Bacillus pyocyaneus* and in 1909 a *Vibrio denitrificans* which are still more active, and which reduce nitrates into nitrites in the same manner as the preceding bacteria. Their harmful action, and also the strong heating of dung, are prevented by sprinkling it after removal from the stable with very dilute solutions of sulphuric acid or with a 1 per cent. solution of hydrofluosilicic acid, which is obtained from superphosphate works (*q. v.*). A fortnight before the manure is spread over the fields it is sprinkled with a dilute (1 per cent.) solution of potassium carbonate in order to neutralise the sulphuric acid. A few litres of fresh stable drainings and of urine are then added and the fermentation is thus immediately re-started, the decomposition of the grosser organic matter being thus facilitated. The admixture of the manure with acid superphosphates or with gypsum containing superphosphates, or the use of beds of peat, had previously been proposed.

Nitrogen is prepared industrially (for example, for the manufacture of calcium cyanamide or synthetic ammonia, for filling incandescent electric lamps, etc.) by the various processes serving to prepare oxygen from liquid air; by the use of improved rectifying columns for liquid air, liquid oxygen of 99 per cent. purity can be obtained and, at the top of the column, liquid nitrogen of 99 per cent. purity. With a less expensive plant, small amounts of nitrogen may be prepared (at a greater cost) by passing air through red-hot retorts filled with copper turnings, which retain the oxygen and leave the nitrogen free. Finely divided copper is obtained by soaking porous cylinders or asbestos with copper salts, heating them, and then reducing the oxide at a red heat (*e. g.*, with hydrogen).

ATMOSPHERIC AIR

Air consists of about four-fifths by volume of nitrogen and one-fifth of oxygen and contains small quantities of water vapour and carbon dioxide, traces of ozone, hydrogen peroxide, and ammonium nitrite, and a very small quantity of the new gases discovered during the last few years, argon, helium, neon, etc. In the lower strata of the atmosphere the most varied micro-organisms abound and cause putrefaction, fermentation, and many other pathological phenomena of great hygienic importance. In the same way as the hygiene of water is looked after, attention to the hygiene of the air would not be less important; the same reasons which oblige us to maintain water free from impurity also apply to the respiration of infected air, or of close atmospheres in which many people are present. Carbon dioxide and many other injurious substances should be eliminated or diluted with pure air. The sterilisation of air with ozone (10 mgrms. per cubic metre) has recently been proposed in special cases, the air being passed through an ozonising fan.

The atmospheric pressure, measured at sea level, is balanced by a column of mercury 760 mm. high (barometer), and since 1 c.c. of mercury weighs 13·6 grms. the pressure of the atmosphere on each square centimetre of surface is 1033·5 grms.; in Eastern Siberia an atmospheric pressure of more than 800 mm. of mercury is frequently observed. At 0° and 760 mm. pressure 1 litre of air weighs 1·29276 grms., that is, 773 times less than water. The specific heat of air is 0·1684 at constant volume and 0·2375 at constant pressure.

The quantitative composition of air was first exactly determined by Gay-Lussac and Humboldt in 1801.[1]

They added to a given volume of air, contained in a eudiometer, an excess of hydrogen, and then passed an electric spark through the mixture. All the oxygen combined with hydrogen in the proportion of 1 vol. of O to 2 vols. of H, and knowing that the diminution in volume was due to two parts of hydrogen and one part (representing the whole) of the oxygen present, and knowing also the initial volume of the air, they deduced the exact volume of nitrogen which remained with the excess of hydrogen. This method of fixing oxygen by an excess of hydrogen had already been proposed by Volta for other purposes.

Still more rigorous experiments, based on another method of absorbing oxygen, were carried out by Boussingault and Dumas in 1811. They evacuated a large flask (20 litres), and after having weighed it, they allowed dry air free from carbon dioxide to enter through a red-hot porcelain tube filled with weighed copper turnings, which combined with the oxygen. The increase in weight of the flask gave the amount of atmospheric nitrogen, while the increase in weight of the copper gave the weight of oxygen which had combined with it to form oxide. In this way they found the percentage composition by weight of air to be 23·095 of oxygen and 76·905 of nitrogen. Since 1 litre of oxygen weighs 1·4291 grms. and 1 litre of atmospheric nitrogen 1·2572 grms., it follows that 100 litres of air are composed of 20·8 litres of oxygen and 79·2 litres of nitrogen.

The volumetric examination may also be made by measuring a definite quantity of air in a graduated glass tube and then introducing a little phosphorus or alkaline pyrogallol solution, which absorbs the oxygen, leaving free nitrogen behind.

Accurate analyses were also conducted later by Regnault and Bunsen, who used the method of Gay-Lussac and Humboldt, and obtained the following still more exact results: 20·95 per cent. by volume of oxygen, and 79·05 per cent. by volume of atmospheric nitrogen, so that 1 litre of air (1·29276 grms.) consists of 0·3 grm. of oxygen and 0·99276 grm. of nitrogen.

The chemical composition of air is found to be almost the same at all points of the earth [according to the experiments of Kreusler, Hempel, Morley, Leduc (1896), etc.], and is as follows, taking the argon into account:

Nitrogen	78·06 %	by volume, or	75·5 %	by weight.
Oxygen	21·00 %	„ „	23·2 %	„
Argon	0·94 %	„ „	1·3 %	„

Air also contains fifteen parts per million of neon, five parts per million of helium, and one part per million of hydrogen (Claude, 1909).

It appears, however, that originally the atmosphere must have had a different composition: Phipson and Koene (1894) believe that when the terrestrial nebula solidified the gaseous atmosphere which remained at that time contained only nitrogen, steam, and carbon dioxide (volcanic), and that oxygen was completely lacking, otherwise the graphite

---

[1] In 1650 Boyle, or rather his pupils Hooke and Mayhow, commenced to show experimentally that air is composed of at least two gases, one of which maintains combustion and life whilst the other does not. In ancient times, on the other hand, it was believed that air was a simple substance. These fundamental conceptions of Hooke and Mayhow, resulting from their lucid experiments, were afterwards forgotten by chemists, and for a century later the greatest confusion reigned with regard to the composition of air and the cause of the phenomena of combustion. It was at this time that the phlogiston theory arose (*see* p. 15).

Priestley, Cavendish, Scheele, Bayen, and, above all, Lavoisier, by means of careful investigation and numerous experiments on respiration, combustion, the oxidation of metals, etc., succeeded in fighting and finally burying the phlogiston theory by determining the true composition of air and by showing that air is actually composed of two constituent gases, oxygen and nitrogen, which are present in a well-defined and constant proportion (Cavendish). During the last few years English chemists have again studied the composition of air by means of very delicate experiments, and have discovered that it contains new gases which had formerly been considered as nitrogen (*see below*).

and sulphides which were then present in the primary rocks would have been oxidised. Under these conditions the origin and gradual development of vegetable organisms, both simple and complex, were perhaps possible, because it is known that plants are anaerobic, that is, they can develop perfectly in an atmosphere which contains only nitrogen, CO_2, and water vapour. By means of plant life the amount of oxygen in the atmosphere was gradually increased and the amount of CO_2 gradually diminished, because vegetable organisms absorb CO_2 and evolve oxygen. With the extension of this vegetative process, and in the course of tens of thousands of centuries, the oxygen slowly increased until the beginning of animal life and its development, which is essentially aerobic, was rendered possible. This form of symbiosis gradually developed until a state of equilibrium was eventually attained between the oxygen emitted by plants but absorbed by animals and the carbon dioxide emitted by the latter and absorbed by the former. The continuity of this equilibrium explains the constant composition of the atmosphere; chemical and physiological processes which fix atmospheric nitrogen are not able to influence it, because these are in turn counterbalanced by other phenomena which liberate nitrogen from various nitrogenous substances (denitrifying bacteria, etc.).

Remembering the enormous masses of oxygen and nitrogen in the atmosphere, it is clear that thousands of years would be required in order to cause any observable modification in its composition, whilst the first exact analyses of the atmosphere were made less than a century ago. We need not therefore fear the near extinction of humanity on account of lack of oxygen, especially as mankind can still live in an atmosphere containing only 15 per cent. of oxygen.

The temperature of the atmosphere at great altitudes is very low, and at the summit of Mont Blanc (4800 metres) it has been calculated by Woikoff and Angot to be — 42°, whilst direct experiments made during the last few years by means of experimental balloons,[1] have shown that it is ordinarily — 5° at a height of 3 km., — 16° at 5 km., — 39° at 8 km., and about — 53° at 14 km. The temperature of space in which our earth moves, outside the atmosphere, is certainly lower than — 100°. Meteorological changes occur more especially in the lower layers of the atmosphere—up to about 10,000 metres (*i. e.*, in the troposphere, beyond which is the stratosphere).

The height of the atmosphere was first calculated by Laplace, who stated that at an altitude 6·6 times that of the terrestrial radius the kinetic energy of the particles of air would overcome the power of gravitation, and that at this point the atmosphere would hence cease, while above it the particles would escape from the earth's attraction.[2]

In 1901 Ekholm found by very exact calculations that the atmosphere should be 70 km. high and that its weight should be about $521 + 10^{13}$ tons, that is, 0·000,000,856 of the weight of the earth.

The atmospheric pressure on Mont Blanc and also on Monte Rosa at 4560 metres is about

---

[1] On November 7, 1916, the aviator Guidi flew at Mirafiori at a height of 7950 metres (world's record), his instruments indicating a temperature of — 32°.

An *experimental balloon* consists of a small balloon of a few cubic metres capacity filled with hydrogen, and with a lifting power of 15 to 18 kilos. The load consists merely of a light cane cage in which automatic registering instruments are placed, namely, a barometer, a thermometer, and a hygrometer, all made of aluminium. This balloon dilates when it reaches high altitudes and bursts at a certain height. The cage then commences to fall from a great height which may exceed 15,000 metres. This fall would be dangerous for the instruments if it were not suitably provided for. A small balloon called the pilot balloon is fixed to the main balloon by means of a cord about 20 metres long and precedes it during the ascent; but, not having sufficient lifting force to sustain the car, it serves to retard the fall, and when the whole arrangement reaches the earth it signals the position of the valuable records by remaining suspended a few metres above the ground. Whoever discovers the balloon and the cage finds sufficient indications in the latter to enable him to consign the whole to the owner, together with a promise of a generous reward. The instruments are almost always returned.

The highest exploration made in this way up to 1911 was 29 kilometres, but on December 17, 1912, an experimental balloon (of Parà rubber, 2 metres in diameter) reached a height of 37,700 metres, at which the temperature was — 51·6° and the pressure only 3 mm.; the lowest temperature was that indicated at 19,730 metres, namely, — 56·9°. Such balloons are made also of paper with a diameter of 3 to 8 metres or even more.

[2] The real limit of the atmosphere appears to be much lower, because on rarefaction and diminution of the temperature of the air, the expansive force of the gas much more easily overcomes the action of gravity. I. C. Schmidt, by supposing that the temperature diminishes regularly with increase of height, finds that the limit of the atmosphere is 58 km. at the equator and 43 km. at the poles.

440 mm., and it is found that at a height of 14 km. the atmospheric pressure is not more than 110 mm. The maximum height to which men have attained in balloons is 10,800 metres (Berson, July 31, 1901), and at such altitudes respiration has to be aided with the help of pure oxygen or preferably of oxygen mixed with carbon dioxide (Mosso).

Some astronomers and physicists hold that at altitudes above 70 to 80 kilometres (pressure 0·0192) the atmosphere changes rapidly in composition and there contains about 55 per cent. of H, 21 per cent. of N, 19 per cent. of geocoronium, and 1 per cent. of oxygen, while at a height of 100 kilometres it would contain 29 per cent. of geocoronium, 67 per cent. of H, and 4 per cent. of helium, and at 500 kilometres 93 per cent. of geocoronium and 7 per cent. of hydrogen.

Geocoronium produces the green lines in the spectrum of polar light.

That atmospheric air, in spite of its constant composition, is not a chemical compound but a simple mechanical mixture, is proved by the following facts: (1) The air which is contained in solution in water has a different composition (35 per cent. by volume of oxygen and 65 per cent. of nitrogen). (2) On mixing nitrogen and oxygen in the proportion in which they are present in air, there is no evolution or absorption of heat. (3) From liquid air the nitrogen evaporates before the oxygen.

The *relative humidity* of air is determined by the hygrometer, and the *absolute humidity* by passing a given volume of air through a weighed tube containing calcium chloride or strong sulphuric acid which absorbs the water.

In air saturated with water vapour at 25° 22·8 grms. of water vapour (absolute humidity) are contained per cubic metre, and on cooling to 0° 18 grms. of this are deposited as rain. Air ordinarily contains only 50 to 70 per cent. of the amount of moisture which it would contain if saturated (degrees of relative humidity).[1]

In order to regulate the quantity of moisture in living-rooms, and especially in workshops, where cotton-spinning, weaving, dyeing, etc., are carried on, and in hospitals in which invalids are exposed to special respiratory cures, it is necessary to take into account not only the relative and absolute humidity, but also the temperature and the humidity which is expelled by the organism during respiration. A healthy man expires 540 litres of air at 37° per hour, producing by means of the oxidation which occurs in the lungs 12·5 grms. of water vapour, that is, 1 cu. metre of the expired air contains 23 grms. of water vapour. Air at 37° is saturated by 43·51 grms. of vapour (*see* Table), so that the air which is inspired from the surrounding atmosphere should contain less than 20·51 grms., that is, 43·51–23 grms., of vapour per cubic metre, in order to avoid the saturation of the air in the lungs themselves during respiration. This is the extreme limit of tolerance, but in order to be able to breathe well there should not be more than 15 grms. of water vapour per cubic metre in the atmosphere, which means that if in an atmosphere we have a temperature of 20° the hygrometer should not indicate more than 87°, because 15 grms. of vapour are 87 per cent. of the vapour of saturation at 20°, which is 17·148 grms.; if the temperature of the atmosphere is 30° the hygrometer should not indicate more than 50 per cent. of saturation, because the 15° of vapour utilised in good respiration are 50 per cent. of the vapour of saturation at 30°, which is 30·079 grms. (*see* Table).

In certain industries, for instance, wool- and cotton-spinning, a certain degree of moisture (vapour, not pulverised water) in the air is necessary, and in order that the temperature may not be raised unduly, especially in the summer, Sconfietti pulverises in the air water from a boiler working at several atmospheres pressure, the evaporation of the hot water and the expansion of the vapour causing cooling as well as moistening of the air.

We give a Table of the absolute humidity showing the number of grams of water vapour which saturate 1 cu. metre of air at various temperatures. This is of service in various practical cases, as may be seen from the foregoing examples.

at 0°	4·869 grms.	at 10°	9·357 grms.	at 20°	17·148 grms.	at 30°	30·079 grms.
„ 1°	5·209 „	„ 11°	9·962 „	” 21°	18·174 „	„ 31°	31·744 „
„ 2°	5·571 „	„ 12°	10·601 „	„ 22°	19·253 „	„ 32°	33·490 „
„ 3°	5·593 „	„ 13°	11·276 „	„ 23°	20·387 „	„ 33°	35·317 „
„ 4°	6·360 „	„ 14°	11·988 „	„ 24°	21·579 „	„ 34°	37·230 „
„ 5°	6·791 „	„ 15°	12·739 „	„ 25°	22·831 „	„ 35°	39·231 „
„ 6°	7·247 „	„ 16°	13·532 „	„ 26°	24·144 „	„ 36°	41·323 „
„ 7°	7·731 „	„ 17°	14·367 „	„ 27°	25·524 „	„ 37°	43·510 „
„ 8°	8·234 „	„ 18°	15·247 „	„ 28°	26·971 „	„ 38°	45·795 „
„ 9°	8·785 „	„ 19°	16·173 „	„ 29°	28·489 „	„ 39°	48·182 „
						„ 40°	50·674 „

---

[1] The hygrometer would always indicate 100° for air *saturated* with water vapour, although the temperature might be different.

The carbon dioxide (CO_2) in the air is detected by shaking the latter with a clear solution of barium or calcium hydroxide, which is rendered turbid by the formation of insoluble carbonate. The CO_2 is quantitatively determined (in the dried air) in the same manner as the moisture by substituting potassium hydroxide for the calcium chloride or H_2SO_4.

Ordinarily 10,000 vols. of air contain 3 to 4 vols. of CO_2 gas, or a larger quantity if the air is impure.

LIQUID AIR

PROPERTIES. Liquid air is a milky liquid, because it contains solid carbon dioxide, but if it is filtered a perfectly transparent, very mobile liquid of a slightly bluish colour is obtained. When it is allowed to stand, nitrogen is first lost and it then becomes blue on account of the excess of oxygen. In this liquid not only mercury is frozen, but also ether and alcohol. Liquid air containing 21·6 per cent. of oxygen boils at 79° abs. (the composition of the vapour is given in the Claude diagram, Fig. 133), that with 60 per cent. at 83° abs., that with 83 per cent. at 87° abs., and that with 98 per cent. of oxygen and 2 per cent. of nitrogen at 90·5° abs.

Combustible substances, for instance, a piece of charcoal or a wooden match, when first lit and then immersed in liquid air burn with very great intensity.

Dewar has found that wood charcoal at the temperature of liquid air has an extraordinary and surprising capacity for absorbing and fixing gases. Thus, if a vacuum of 2 to 3 cm. is made in a Crookes tube which communicates with a receiver containing charcoal, the electric discharge at first has the usual violet colour. If the charcoal is now cooled from outside by means of liquid air the air remaining in the tube is gradually absorbed by it, and the electric discharge assumes all the colours which are seen in a Geissler tube until the vacuum increases so much as to give the beautiful greenish-yellow fluorescence due to the impacts of the electrons: when all the central portion of the cathodic bundle is fluorescent we have a true Crookes tube as used for radiography; the vacuum still increases, however, up to ten one-millionths of an atmosphere, and the tube then becomes dark because the current is unable to traverse it.

Under the action of liquid air rubber becomes as brittle as glass; meat, eggs, and flowers become hard and can be reduced to powder; nickel steel at these low temperatures becomes magnetic; the electric resistance of metals diminishes rapidly and becomes almost zero in liquid air, so that we may obtain ideal electric conductors without resistance if the wires are immersed in liquid air, especially as it is also a perfect insulator. The heat of evaporation of a kilo of liquid air is 125 Cals. Attempts have been made to destroy the germs of infectious diseases by means of liquid air, for instance, the bacilli of typhoid and diphtheria, but with negative results, the spores of these microbes regaining their activity—even after being in contact with liquid air for several months—as soon as they are brought to the ordinary temperature.

When liquid air is poured directly on to the dry skin no burns are produced, as it assumes the spheroidal state, and the part which evaporates prevents contact with the skin, and one experiences merely a sensation of a slight electric discharge; if, however, the skin is wet burning occurs, but this is only superficial, because the layer of ice immediately formed insulates the parts underneath. If the skin is rubbed with a little wadding soaked in liquid air a white spot is first formed, but this soon acquires a bright colour, and the blood which was first driven from the spot flows back to it. If the refrigeration is prolonged the points exposed to it become as hard as ice. Surgical operations performed after such treatment have given brilliant results; healing was very rapid, and there was a complete absence of pus.

By means of the cold produced by the evaporation of liquid air, petroleum, alcohol, and oil of turpentine are easily frozen; alcohol no longer burns under such conditions, but becomes dense and finally an amorphous solid; ether crystallises; yellow phosphorus acquires a crystalline structure and loses its property of becoming luminous in the dark. From liquid air and red phosphorus an explosive mixture is obtained.

In the air liquid air produces fumes through the condensation of atmospheric moisture. Various organic and inorganic reactions are caused or prevented by liquid air.

Liquid air cannot be preserved in closed steel cylinders under pressure in the same way as liquid carbon dioxide, because its critical temperature is at — 140°, and above this point it cannot exist in any other state than as a gas, whatever the pressure may be, so that above this temperature no closed receptacle would be able to resist the pressure.

Liquid air is therefore used on the spot or for the production of oxygen, or it may be kept or despatched in small quantities in open double-walled bottles in which there is a vacuum between the two walls and the inner sides of which are coated with silver. With these bottles, which were devised by Dewar (Fig. 127) and by D'Arsonval, the heat rays from outside are reflected and the liquid air in such open bottles, containing two to three litres, slowly evaporates at the rate of 15 to 20 c.c. per hour and lasts for three to four days. For experimental purposes liquid air is placed in Weinhold tubes of glass with triple walls (Fig. 128). In order to transport liquid air over long distances without danger of breaking the flasks (flasks to hold 2 litres cost from 12*s.* to 20*s.*) metallic cages are used (Fig. 126) in which the flask, which has been previously wrapped in wool or felt, is placed. When liquid air is poured from such a bottle the neck should be enveloped in a piece of cardboard, which is a bad conductor of heat, and sharp fluctuations of temperature which might break the flask are thus avoided.

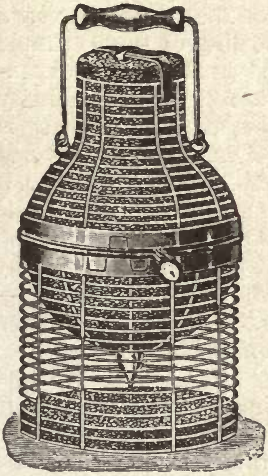


Fig. 126.

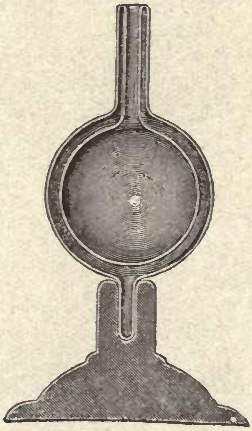


Fig. 127.

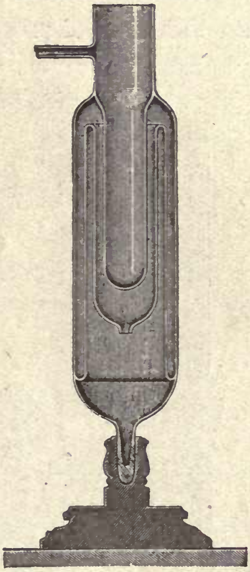


Fig. 128.

PREPARATION. (*See also* Liquefaction of Permanent Gases, p. 29; and of Oxygen, p. 196). The first Linde apparatus for the liquefaction of air was introduced into Italy in 1900 by the Society for the Encouragement of Arts and Manufactures (Milan), and was able to produce one litre of liquid air per hour (Fig. 129).

This apparatus is provided with two pumps, *e* and *d*; the former aspirates the outer air and forces it into the latter at a pressure of twenty atmospheres, and the latter then compresses it to 200 atmospheres in a cylinder, *f*, which separates the water used for the lubrication of the pistons in the pump cylinders. The air is heated by the compression and is passed through a coil arranged in a refrigerating box, *g*, containing ice and salt;

it then passes when compressed through a triple concentric coil of stout copper (*see* figure at side). In the lower portion of the central coil is a valve, *a*, which permits the compressed air to expand rapidly to twenty atmospheres; it then rises through the second coil which surrounds the first one and reaches the pump, *d*, through the tube *p′*, to be again compressed and allowed to expand. Each expansion lowers the temperature considerably and the cooled expanded air, passing through the coil in a contrary direction to the air which arrives, acts as a refrigerator for the latter. The temperature finally reaches — 189°, and then in expanding a large part is liquefied and is discharged through the valve *b*, into a double-walled glass flask, *c*. The space between the two walls is evacuated, as by this means liquid air can be kept for a long time; it may also be poured into other Dewar bottles (described above).

Linde (like Cailletet before him) calculated the efficiency of his liquid air machines from the formula of Joule and Thomson on the cooling of expanding gases; this cooling is equal to $0{\cdot}276\ (P_1 - P_2)\left(\frac{273}{T}\right)^2$, where $P_1 - P_2$ indicates the difference of pressure (in atmospheres) before and after expansion and T the absolute initial temperature. According to this formula, by starting at 0° with gas compressed to 250 atmospheres, a cooling of — 69° should be produced on expansion to the ordinary pressure; if the air is originally at — 141° and at 250 atmospheres, a temperature of — 294° should be obtained on expansion, whilst by starting at — 194°, — 423° should be obtained on expansion.

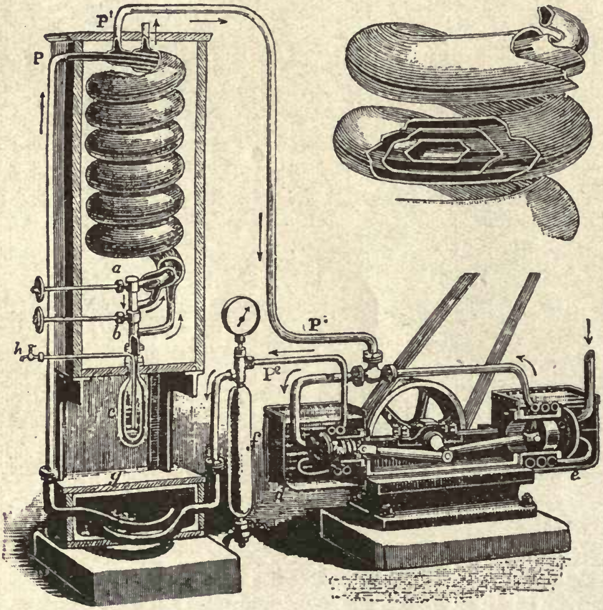


Fig. 129.

Mewes in 1901, Pictet in 1903, and Mix in 1901 and 1908, showed that these results are erroneous, and that the formula of Joule and Thomson cannot be applied, because it presupposes that the expansion occurs exclusively at the cost of the so-called internal energy, whilst in this case, on the contrary, the work performed is entirely external, as it is exercised by the gas in expanding against the atmospheric pressure, that is, in changing to a greater volume, and the lowering of the temperature produced in performing this work may be calculated from simple physical laws (*see also* pp. 27 and 51). The results of such calculation coincide with practical experience; a gas which expands from 250 atmospheres up to 1 atmosphere would be cooled as follows: Starting from 0° the temperature would descend to — 61°, starting from — 141° we should reach — 170·5°, and starting from — 194·5° we should reach — 212°. The discussion of this question lasted for years, and in 1907 Kozic confirmed Linde's hypothesis on the internal work, admitting, however, that the Joule-Thomson formula is not applicable to all gases, especially not to air, and must be modified. Claude still insists that the cooling is due also to external work, more especially in the cases of gases which are not perfect, and that air under these circumstances is not a perfect gas.[1]

The principal *industrial uses of liquid air* are at present only three in number, namely, the economical preparation of oxygen, of nitrogen, and of explosive materials.

Another application of liquid air consists in the preparation of *oxyliquit*, which is a powerful explosive formed by rapidly mixing liquid air, rich in oxygen, with powdered charcoal, petroleum residues, or cotton wool. The mass is placed in cardboard capsules forming cartridges, and these are exploded by means of an electric fuse and a cap of mercury fulminate. After a quarter of an hour the oxyliquit loses its explosive power because the liquid air partially evaporates. For boring the Simplon tunnel a machine was first used which produced 150 kilos of liquid air daily for the manufacture of oxyliquit, and gave good results, but it was abandoned on account of the great urgency of these boring operations. Oxyliquit has also been used as an explosive in certain work at Powzberg, in Upper Bavaria, and for large mining operations. It costs about 5*d*. per kilo. Better results were obtained (1914) by mixing the liquid air with gun-powder. In an English colliery the explosive effect produced by enclosing liquid air in an iron tube which is introduced into the coal seam has been used by allowing the temperature of the whole mass of liquid air to become higher than the critical temperature; the tube then explodes whatever may be the pressure, because the air is gasified and exercises a pressure of 5600 kilos per sq. centimetre, thus dislodging as much as 30 tons of coal by means of the discharge.

The oxygen obtained from liquid air has been applied by the Rhenania Company of Aix-la-Chapelle for the preparation of chlorine by Deacon's process.

Among the future applications of liquid air one may foresee the tempering of steel at low temperatures by immersing it whilst hot in liquid air, and thus making it very much harder. In 1913 liquid air was suggested as a means of drying certain foodstuffs without altering their taste, smell, and colour, the materials being frozen by the liquid air, powdered and then dried slowly in a vacuum at about 0°.

The manufacture of liquid air may become of immense importance if the prophecy of Pictet that by this means oxygen will be obtained at a tenth of a penny per cubic metre were realised. Thus it could then be advantageously applied for lighting purposes by mixing coal-gas with oxygen, and producing an extremely powerful Auer light which, according to Pictet, would achieve an annual economy of £2,000,000, if applied in the city of Paris alone. At

---

[1] On the basis of new experiments, Linde, in 1911, confirmed his views and asserted that, if the theory of the external work of compressed gases were accurate, this work expended in the displacement of atmospheric air should be the same for all gases under identical conditions of temperature and pressure. Experiment shows, however, that such work varies with the nature of the gas and that when compressed hydrogen is allowed to expand at the ordinary temperature no cooling, but heating, occurs, cooling of the gas being observed only in the interior of the bomb. Further, if the cooling were the consequence of work done, its extent should diminish with diminution of volume and with fall of the temperature, whereas in reality it increases with lowering of the temperature owing to increase of the internal work resulting from the diminished volume. Experiments specially carried out in the physical laboratory of Professor Knoblauch at Monaco demonstrate that the influence of the absolute pressure on the cooling of expanding gases harmonises sufficiently well with the results of the van der Waals formula. Investigations made with air and with oxygen show that, for oxygen the cooling is 12 per cent. greater than for air; the latter was studied at 15°, — 30° and — 45°, the data obtained for the last of these temperatures being in poor agreement with the temperature functions foreseen by Joule and Thomson, according to which the cooling should increase in inverse proportion to the square of the absolute temperature.

When compressed hydrogen at temperatures down to — 116° expands it becomes heated, so that, in order to bring about liquefaction, it is necessary to cool the gas to — 116° before applying the usual process of compression and expansion.

this price it would be possible to use oxygen extensively for metallurgical purposes, perhaps even in blast-furnaces for the direct production of wrought-iron without the necessity for Bessemer converters, and in the converters themselves the operation would be rendered more perfect and more rapid. The autogenous welding of large structures of wrought-iron, such as bridges, girders, boilers, etc., would then become very common. Other industrial applications have already been discussed in the chapter on Oxygen.

The use of liquid air in motors was also prophesied, but it has now been shown that liquid air as such is not an economical source of motive power because from 14 cu. metres of air by repeated compressions and expansions about 900 grms. of liquid air are obtained, and this gives only 700 litres of gas on expansion, so that the effect thus obtained is twenty times smaller than that which would be obtained by utilising 14 cu. metres of compressed air directly without liquefying it. On the average liquid air is capable of giving up 4 per cent. of the energy employed during its liquefaction.

Further, there can be no industrial importance in the use of liquid air as a refrigerating agent, because 1 kilo of liquid air produces the same refrigerating effect as $1\frac{1}{2}$ kilos of ice, and whilst at least 100 h.p.-hours are required for the production of 50 litres of liquid air, only 3 h.p.-hours are required for the production of 75 kilos of ice (the heat of fusion of ice is 79 Cals. per kilo, and 1 kilo of ice costs less than a tenth of a penny, whilst 1 kilo of liquid air costs at least 4*d*.).

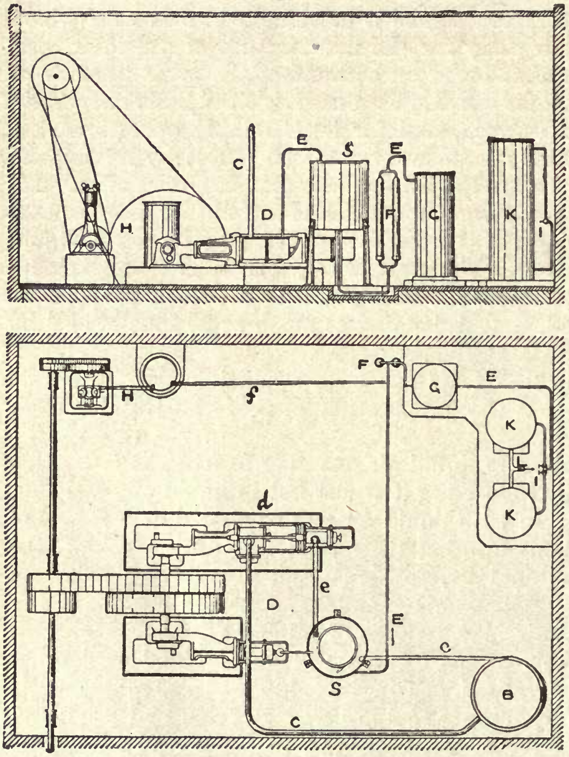


Fig. 130.

During gasification 1 kilo of liquid air is able to cool about 30 cu. metres of air from 20° to 10°.

As a refrigerating agent it is only of importance for laboratory use, in cases where temperatures very much lower than 100° below zero are to be obtained.

The industrial *manufacture of oxygen and nitrogen* is to-day carried out almost exclusively with liquid air, using various processes, of which we shall illustrate the most important, those of Linde, Pictet, and Claude, because these three are at present competing for predominance in this industry, which is continually acquiring greater importance in Italy and other countries.

H. Siemens in 1857 and E. Solvay in 1884 were the first to attempt to liquefy air by means of compression and expansion together with the production of external work. When, however, very low temperatures were reached (in the case of Solvay — 92°) the machine used to produce work by expansion of the gas no longer acted at these temperatures, as no lubricant was then known which was able to prevent excessive friction. During recent years Claude has found that petroleum ether serves very well because it does not solidify until nearly — 200° (even at —100° it is dense like a lubricating oil), and when the production of liquid air is once started this forms a suitable lubricant, although it is not completely satisfactory.

I. MANUFACTURE OF OXYGEN AND NITROGEN BY THE LINDE PROCESS.

The Linde patent of 1889, which referred to the liquefaction of air only, was followed by the patent of 1895 (Ger. Pat. 12,528) for the fractional evaporation of air with the object of separating oxygen and nitrogen. As regards priority of patents, note must be made of W. Hampson's English patent 7559 (1896), Lesueur's Canadian patent 74,430 (1900), and R. Pictet's U.S. patent 677,323 (1901). In 1902 Linde took out a new patent for a rectifying apparatus with which oxygen was obtained under still more favourable conditions. On account of a series of objections by Pictet, Levy, Mix, and others, the German patent was only conceded in May 1906 (Ger. Pat. 175,620). A more perfect type of Linde plant has also been at work in Milan since 1905, and we give a diagrammatic illustration of it in Fig. 130.

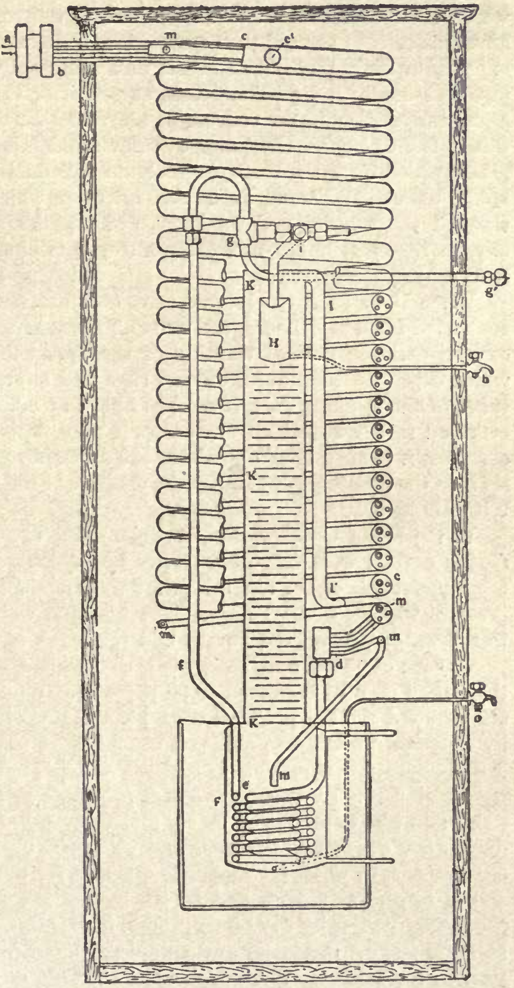


FIG. 131.

The air is aspirated from outside and compressed in *d* to a pressure of about 5 atmospheres, by which means it is heated to 40°–50°. It then passes through the coil, *e*, immersed in a refrigerator, *S*, and is afterwards freed from CO_2 by passing it through a double purifier, *B*, filled with slaked lime moistened with a little sodium hydroxide solution. It passes through a tube, *C*, into the other portion of the compressor, *d*, where it is compressed to 35 atmospheres, still in iron tubes, and since it is thus heated to 50°–60° it is again cooled in an ordinary water cooler, *S*. It is now compressed to 180 atmospheres in *D*, and as it is thus heated to 60°–70° it is again cooled by water in the cooler, *S*; from here it passes through the tube *E* and through two dryers, *F*, containing lumps of fused calcium chloride and is then cooled to —15° in *G*, where there is a double concentric coil in the interior of which the compressed air passes in one direction while ammonia passes during expansion through the outer tube in the opposite direction; this ammonia issues from an ordinary ice machine, *H*, to which it returns through the double tube *f*.

The air, compressed to 180 atmospheres and at a temperature of —15°, enters one of the two rectifying columns, *K*, through a distributing cock, the other rectifying column being kept in reserve. The air first enters through the tube *a* (Fig. 131), which divides into a triple coil of copper, *b*, enclosed in a large tube, *c*, which runs spirally round the whole of the rectifying column. At the base of the triple coil the three tubes reunite to form a single tube, *d*, which is then bent into a coil, *e*, in the interior of the sheet-iron vessel, *F*, and continues its course upwards in the tube *f* to the valve *g*, which regulates the expansion of the air from 180 atmospheres to a pressure one-fourth of an atmosphere above the atmospheric pressure; this valve is regulated by the key, *g′*. The expanded air is considerably cooled and passes into the small reservoir, *H*, which is placed at the top of the rectifying column, *K*; from here it then passes through the tube *l*, which carries it downwards to *l′*, where it enters the large tube, *c*, and rises in a contrary direction to the triple coil, which it surrounds and which carries the compressed air. The expanded air escapes above through *c′* at −15°, *i. e.*, at the temperature of the compressed air which enters, and serves to cool a part of the coil *G* (in the preceding Figure) of the ammonia refrigerator; it then escapes into the atmosphere at −5° to −6°. The air which expands at the top of the column is thus continually cooled more and more before expanding, and finally it liquefies. This occurs after the apparatus has worked for about an hour, and the liquid air collects in the vessel *H*, which holds from 3 to 4 litres. When this is full of liquid, the latter overflows and falls over the numerous perforated copper plates which form the rectifying column and finally collects in the large vessel, *F*, which holds about 30 litres. It is the nitrogen which mainly evaporates, and this rises through the column, and the shower of liquid air which descends abstracts what little oxygen remains in the ascending nitrogen, which thus escapes almost pure from the tube *l*.

When 10 or 12 litres of liquid have accumulated in *F*, which is the case after work has continued for 6 or 7 hours, the remaining liquid contains from 96 to 98 per cent. of pure oxygen and the normal working of the apparatus commences. Through the tube *m*, which dips into the liquid, oxygen rises and is gradually gasified, passing up one of the tubes of the triple spiral; it escapes above at *m′*, at a temperature of about −5°, and is collected in a gasometer from which it may be passed into suitable compressors, which compress it in steel bombs to about 130 atmospheres pressure. When normal working has set in in the rectifying apparatus, the pressure of the air is no longer kept at 180 atmospheres, but only at 90.

In the Milan works the original plant (the capacity has now been doubled) produced, during normal working, 6 cu. metres of oxygen per hour, about 21 h.p. being used for the liquefaction of the air, 3 h.p. for the ammonia ice machine, and 3 h.p. for the compressors which fill the bombs. The machine works day and night, and there are two workmen, one to fill the bombs and the other to supervise the machinery.

Oxygen of 95 per cent. purity is thus obtained, and by reducing the output by one-fifth the purity may be increased to 99 per cent. Whilst 12 kw.-hours, that is, 16 h.p.-hours, are required for the production of 1 cu. metre of oxygen and 2 cu. metres of hydrogen by electrical means, to produce 1 cu. metre of oxygen with a small Linde machine only 5 h.p.-hours are required. In plants which produce 5 cu. metres of oxygen per hour with 20 h.p. the oxygen costs 3·84*d.* per cubic metre, excluding sinking fund and patent rights; in plants producing 50 cu. metres with 100 h.p. it costs 1·35*d.*, and in plants producing 500 cu. metres per hour and using 800 h.p. it costs 0·58*d.* per cubic metre. The consumption of water for cooling is different for the three above-mentioned types of plant, and is respectively 1, 4, and 30 cu. metres per hour. There are to-day several works producing oxygen by the Linde process in Barmen, Berlin, Paris, Birmingham, and Milan. In Paris 600 cu. metres of oxygen are produced per day. There is a new Linde plant in Italy in the calcium cyanamide works at Piano d'Orte which also utilises all the nitrogen obtained by liquefying 3000 cu. metres of air per day. At Naples and Genoa new works for the production of oxygen from liquid air by the Linde and Claude processes have recently been erected.

II. PICTET'S PROCESS. In February 1900 and in July 1901 Pictet took out patents for the liquefaction of air, by employing various cooling liquids and then separating oxygen from nitrogen by heating the liquid air by means of atmospheric air at a pressure below twenty atmospheres and near its liquefying point. Owing to the opposition of Linde and others, the Pictet patent was conceded only in March 1905 (Ger. Pat. 1,652,682 ?). This process differs from Linde's process more especially by the fact that in the Pictet apparatus there is no intimate contact between the heating mass (cold compressed air) and the liquid air, as the two substances flow through distinct channels, one of which surrounds the other, but which do not communicate.

Pictet's apparatus is diagrammatically illustrated in Fig. 132. The air is aspirated and compressed by the compressor *k*, and passes through the coil *c*, arranged in a circular tank, *a*, in which Pictet's refrigerating liquid (sulphur dioxide and carbon dioxide) circulates in a contrary direction through another coil, *f*. The vapours of the refrigerating liquid are collected again by the compressor *g* in order to be liquefied again and repassed through the system. The compressed air is thus cooled to — 80°, and passes into the coil *c*, immersed in the circular vessel, *b*, which is filled with alcohol, the vapours of which are rapidly collected by the compressor *t*, to be liquefied and again sent into circulation. In this way the compressed air is cooled to — 140° and then enters the spirals, *d*, which are surrounded by the vapours of liquid air which has collected on the bottom of the central reservoir. The air here liquefies and accumulates at the base together with the air already liquefied. By allowing this air to evaporate partially, the vapours evolved, which consist mainly of nitrogen, are made to work a gas turbine, *y*, in order to recover a part of the work by turning the shaft of a dynamo, *r*. The remaining liquid yields oxygen.

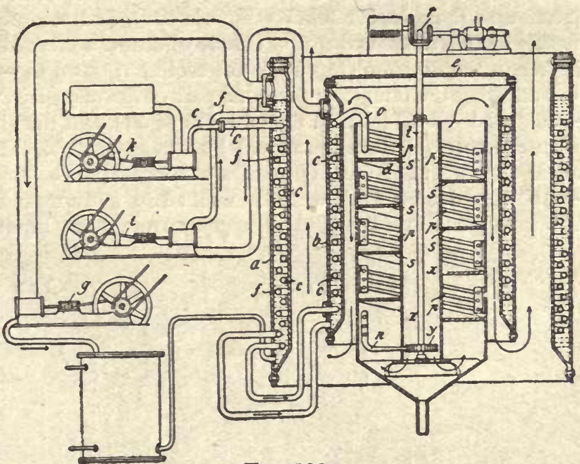


Fig. 132.

III. CLAUDE'S PROCESSES. The question whether nitrogen or oxygen is first liquefied during the liquefaction of air was much discussed by scientists. Linde and Dewar stated that the liquefaction of the two gases occurred simultaneously, and Pictet believed for a long time that the nitrogen was liquefied before the oxygen. Lesueur maintained the contrary opinion, and in 1903 G. Claude produced experimental proof that the oxygen is liquefied first and then the nitrogen; he showed also that evaporation occurs in the reverse sense and that the nitrogen evaporates before the oxygen. Claude also published a curve (Fig. 133) showing the composition of the vapours given off by liquid air containing various proportions of oxygen. The upper curve starting from *A* shows the composition of liquid air from 20·8 per cent. of oxygen (20·8 per cent. being the amount present in air), and the composition of the vapours formed from such air is given by the lower curve, *D*, which starts with 7 per cent. of oxygen. As the liquid air contains more and more oxygen as indicated by the curve *AE*, which goes up to 100 per cent., the vapours are also correspondingly richer in oxygen, as indicated by the curve *DE*. Vapours containing 20·8 per cent. of oxygen (point *C*) are formed from liquid air containing 47 per cent. of oxygen; in order to obtain liquid oxygen it is therefore unnecessary to liquefy all the air.

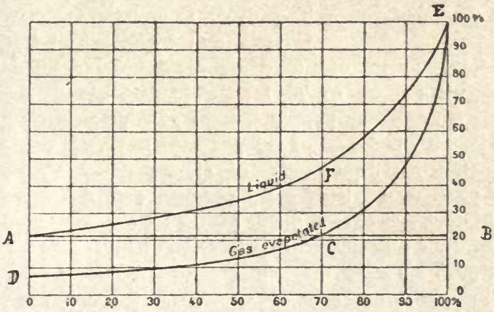


Fig. 133.

In 1903 Claude invented an apparatus for rectifying liquid air which is based on these results and is analogous to that of Linde, but with this difference, that he condensed the oxygen and the nitrogen apart; the former, when liquefied, is introduced into the rectifying column at two-thirds of its height, where it falls in the form of a spray, giving up to the vapours which rise almost all its oxygen, so that at the bottom of the column there is pure liquid oxygen, whilst at the top nitrogen vapour collects in an almost pure state. With other processes, which liquefy all the air, the escaping nitrogen always carries away 7 to 8 per cent. of oxygen, this representing the composition of the vapour indicated by point *D* of the diagram.

In June 1906 Claude finally invented a new and ingenious modification, namely, that of expansion by means of external work based on the principle that the work performed by the compressed gas is greater the higher its temperature, and therefore smaller the further removed the gas is from the point of condensation or from the state of vapour (in which latter case it no longer follows Boyle's law), and the nearer it is to a perfect gas. By means of this *compound system* Claude obtained a gradual expansion of compressed air, as is seen in the diagram (Fig. 134), not cooling it down to — 190°, as in the other processes, but allowing the temperature of one part of the partially expanded air to oscillate between —160° and —140° (critical temperature of air), and liquefying further air compressed at 40 atmospheres (critical pressure) by means of this. The compressed air which enters at *M* expands in *A* until it reaches a temperature below the critical point, for example, — 160°, producing work which is utilised in *P* by means of a turbine or other machine. Air thus partially expanded then passes round the liquefier, *L*, which is fed with compressed air at 40 atmospheres; this liquefies at a temperature of — 140°, and may be discharged through the cock, *R*, while the air surrounding the liquefier is heated from — 160° to — 140° and expands completely in *B*, the work being utilised in *P*, and a further cooling produced which causes the air in *L′*, compressed to 40 atmospheres, also to liquefy in the same manner as that in *L*. The expanded air is cooled to — 140° and cools the air in the generator, *M*, so that this arrives in the expander, *A*, at a temperature of — 140°. The cycle thus becomes continuous, and by means of this process Claude claims to have prepared 0·850 litre of liquid air per h.p.-hour. This yield, however, refers to a plant which utilises 60 to 70 h.p. over and above the recovered work, and assumes that the air compressors supply 6 kilos of compressed air at 40 atmospheres per h.p.-hour (that is, an efficiency of 66 per cent.). With other forms of apparatus which produce spontaneous liquefaction of air at the ordinary pressure and therefore at — 190°, the yield is 0·2 litre per h.p.-hour, and for those which liquefy air under pressure the yield does not exceed 0·660 litre. By the combined system the possibility is given of lubricating the machine with petroleum ether (pentane), which is a much better lubricant than liquid air itself.

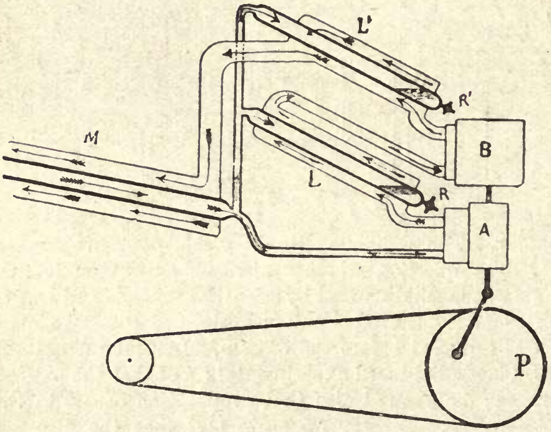


FIG. 134.

At Boulogne-sur-Seine two plants are working, one of which produces 700 cu. metres of oxygen and the other 1000 cu. metres daily of a strength of 96 to 98 per cent.

In 1909 Claude added 0·5 grm. of alcohol per cubic metre to the air to be liquefied in order to enable it to be more easily dried, as the alcohol which condenses when cooled also carries down with it all the remaining moisture.

Of the numerous patents granted in different countries during recent years for the preparation of oxygen and nitrogen from liquid air, only those will be mentioned here which have found or probably will find application in practice. Most of the others refer to small modifications in the details of apparatus or processes already known and are often evident attempts (not always successful) to elude other patents.

In 1908–1910 Hildebrandt endeavoured to improve still further the rectification of liquid air. His system was first applied in a large works in Berlin[1] and then spread rapidly, so that, while the Linde Company fitted up 60 oxygen works prior to 1911, Hildebrandt erected 50 plants during the years 1908–1912.

Jänecke (Ger. Pats. 220,270 of 1908 and 246,341 of 1910) attempted to simplify the process of separating the oxygen from the nitrogen of liquid air by means of a rectifying column of new type and vacuum distillation.

E. F. Aumont (Ger. Pat. 260,758, 1911) obtained liquid air and resolved it into its components by a rectifying column on the ordinary system, the heat dispersed being counterbalanced by expansion of hydrogen.

A. Neumann (Ger. Pat. 281,518, 1913) suggests an ingenious but complicated improvement of the rectifying tower for liquid air.

Mix and Heylandt propose a process which apparently allows of the preparation of 2 litres of liquid air per h.p.-hour.

H. Barschall facilitates the separation of the oxygen from the nitrogen in an ordinary liquid air apparatus by means of reduced pressure (Ger. Pat. 259,877, 1911). Jänecke (Ger. Pat. 220,270, 1908) works similarly. The Mewes system (Ger. Pats. 222,840 of 1907 and 242,867 of 1909) also appears to have practical application.

Liquid air is manufactured in France by the Claude and Linde systems, in Germany by the Linde, Pictet, and Hildebrandt systems, etc., in England by the Hampson, Linde, and Pictet systems, and in America by the Linde-Tripler process. In Italy there are three industrial plants using the Linde process, two using the Claude process, and one the Hildebrandt process, while others are projected.

UTILISATION OF ATMOSPHERIC NITROGEN

One of the problems which occupy the chemical and agricultural world to-day is that of nitrogen. Agriculture alone consumes 75 per cent. of the two most important sources of nitrogen compounds which nature and industry place at the world's disposal, namely, nitrate and ammonium sulphate. The extraordinary progress made by agriculture during the last forty years is closely connected with the growing consumption of artificial manures which were first proposed by Liebig in order to maintain or increase the fertility of the soil (*see* Chapter on Chemical Fertilisers and Superphosphates, Part III).

If agriculture may maintain its present tranquil attitude in so far as the source of phosphates and potassium salts necessary for the soil and for the plants is concerned, it is otherwise with the most important problem of the restoration to the soil of all the nitrogen which is abstracted from it by the various crops to be transformed into vegetable albuminoid matters for the feeding of animal organisms, including man.

Plants are not able to obtain their nitrogen directly from that immense and inexhaustible store, the atmosphere, and are not even able to absorb nitrogen directly from the ammoniacal compounds present in the soil, as these must first be nitrified before assimilation (*see below:* Biological process).

The largest source of combined nitrogen for agricultural purposes was found in the important deposits of nitrate in Chili, which were discovered in 1830 and have been

---

[1] The cost of oxygen prepared by the Hildebrandt process, excluding the general expenses and sinking fund, and neglecting the value of the nitrogen obtained is as follows: (I) for a machine giving 5 cu. metres of liquid oxygen per hour (120 cu. metres per 24 hours), and (II) for one giving 20 cu. metres per hour (480 cu. metres per 24 hours). The daily outlay is:

	I	II
Power	10·72*s.*	40·32*s.*
Three operatives	12·00*s.*	12·00*s.*
Lubrication	0·80*s.*	1·60*s.*
Chemicals to remove CO_2 and H_2O	0·24*s.*	0·48*s.*
Cooling water for the compressors (I) 24 cu. metres (II) 60 ,, ,,	3·84*s.*	9·60*s.*
Total	27·6*s.*	64·0*s.*

Thus, 1 cu. metre of liquid oxygen will cost 2¾*d.* in case I, and 1⅗*d.* in case II. With larger plant the cost is reduced still further.

enormously utilised for agricultural purposes since 1860; from that time very large quantities have been imported into Europe.

In 1860 Germany alone imported 6700 tons; in 1880 the figure rose to 55,000 tons, in 1900 to about 550,000 tons, and in 1909 to more than 665,400 tons. In 1908 the whole of Europe consumed 1,635,000 tons of a value of about £15,000,000; Italy imported 8500 tons in 1890, 40,500 in 1900, 43,780 in 1903, and 60,784 in 1908.

Although the consumption of nitrate was so enormous, only a few years ago was it realised that there was a serious danger of the exhaustion in a short time of the valuable deposits of Peru and Bolivia. If the consumption continues in its present proportions there will be no more nitrate in Chili after forty or at most fifty years, and this would constitute a veritable calamity not only for agriculture, but for the whole of humanity.

Attention was therefore directed to other sources of nitrogen and it was at first thought that the *ammonium sulphate* obtained in the manufacture of lighting gas and metallurgical coke, which had almost the same fertilising power as nitrate, might supply the growing needs of modern agriculture. In spite, however, of the increasing world's production of this ammonium salt, which rose from 10,000 tons in 1860 to 570,000 tons in 1903 and 900,000 tons in 1909, no sufficient quantity to satisfy the ever-increasing needs of modern agriculture could be obtained (*see* chapter on Ammonium Sulphate in Part III of this volume).

During the last few years the talents of numerous scientific men have been directed to research on some new method of utilising atmospheric nitrogen and these researches have led to three new practical processes for the fixation of this inert gas in the form of fertilising nitrogen compounds.

FIG. 135.

(*a*) **BIOLOGICAL PROCESS.** It is now generally admitted—as Boussingault concluded from his early experiments—that plants do not directly fix the free nitrogen in the atmosphere, and that even the larger part of the ammoniacal compounds found ready formed in the soil are not directly absorbed by plants; before assimilation they have to undergo a process of nitrification underground. This important and beneficent work is carried on by certain bacteria which are always present in the soil. In 1891 Winogradsky discovered and studied two species of bacteria, one of which oxidises ammonia and ammonium salts, transforming them into nitrites, while the other oxidises the nitrites, transforming them into nitrates, which are directly assimilable by the plant. Only the potato and certain plants which live in acid soils assimilate ammonium salts directly. In 1853 G. Ville had already observed and maintained, against the general opinion, that in the case of certain plants, especially the Leguminosæ, more nitrogen is present at the end of growth than was present in combination in the soil, and that therefore a portion of this must have been provided by the atmospheric nitrogen. On account of the hostility of Boussingault and Dumas the work of Ville was not seriously considered until 1886 when Hellriegel showed experimentally that the papilionaceous Leguminosæ were able to fix considerable quantities of atmospheric nitrogen and that this process was especially active when their roots showed numerous small nodules formed of accumulations of bacteria (*Bacterium radicicula*, Fig. 135), which were always found more or less abundantly in the soil. These nodules were not formed in sterilised soil and the growing plant was then stunted and remained dwarfed.[1]

---

[1] G. Briosi (1910) showed by rigorous experiments that Boussingault's theory cannot be generalised or accepted too dogmatically and that various plants—cryptogams and phanerogams—even in media kept sterile during 40 days (or longer) of culture, can fix atmospheric nitrogen directly (without the intervention of bacteria), when they have no nitrogenous matter at their disposal.

This is thus a case of true symbiosis: the plant lives and prospers through the vitality of these bacteria. Hellriegel and Wilfart in 1891 and also Breal, Schlösing, Laurent, etc., confirmed this important function of these bacteria which fix atmospheric nitrogen. This nitrogen is elaborated by these organisms and is transformed into compounds which are easily assimilated by the roots of the plants.

For more than two thousand years it had been noticed that the fertility of the soil could be increased by the repeated cultivation of Leguminosæ on the same portion of ground, but the cause of this phenomenon has only now been explained. The two most closely studied species of the *azotophagic bacteria* or *nitrogen bacteria* are *Clostridium Pasteurianum* of Winogradsky and Beijerink's *Azobacterium;* during the last few years several other species have been described, and it appears from these that they are not true bacteria, but parallel and more or less colourless forms of *Cyanoficia.*[1]

In 1894 the firm of Meister Lucius und Brüning of Höchst (near Frankfort), after work and experiments expressly conducted by Professor Nobbe, placed on the market *nitragine*, which is a pure culture of these useful bacteria, and when spread over the soil renders the ordinary fixation of nitrogen more active. It was calculated that in a million hectares of good soil the bacteria naturally present annually assimilated as much nitrogen from the atmosphere as would be worth £3,200,000 and that by the addition of pure cultures of nitrifying bacteria these soils should be able to fix at least a quarter more nitrogen, showing a gain of more than £800,000.

Favourable results were, however, not obtained on all soils by the use of nitragine, and the bacteria often succumbed in the struggle for existence with the numerous harmful bacteria already present in the soil. Sometimes, too, nitragine was wrongly employed by the farmers, and its failure was then complete.

For these reasons Moore, in America, prepared more powerful cultures of these bacteria by cultivating them on slices of potato instead of in broth, and then drying the cultures on cotton wool. Professor Remy, in 1907, has shown, however, that this dried American nitragine completely loses its activity, whilst that preserved in agar or in gelatine according to Hiltner's method has been shown to be more effective for the formation of leguminous nodules in the plants.[2]

Of 98 experiments made with nitragine in Bavaria in 1903, 81 gave markedly favourable results, 9 were uncertain, and 8 were negative. In Italy Moore's cultures did not give very favourable results, although in the case of French bean cultivation they produced

---

[1] Löhnis and Westermann in 1908 proposed that these bacteria should be divided into four groups: (1) *Azotobacter chroococcum*, characterised by the blackish-brown colour of its agglomerates when in thick layers. (2) *Azotobacter Beijerinckii*, which when present in the form of sarcina has a yellow colour. (3) *Azotobacter agile*, which is highly motile and fluorescent. (4) *Azotobacter vitreum*, which is non-motile, of globular form, and accumulates in transparent mucilaginous layers.

[2] Professor Bottomley, of London, gives the following instructions for the inoculation of soil or seeds with nitragine, which comes on to the market in small boxes containing two or three packets: the packets containing the nutrient salts are dissolved in a tub in 4 to 5 litres of cold but previously boiled water. The packet containing the nitragine culture is then added; the tub is covered with a cloth, and allowed to stand in a tepid place at 24° to 27° for twenty-four to thirty-six hours. The liquid becomes milky when the bacteria have developed and multiplied well. The seeds are then moistened with this liquid and are allowed to dry in the shade before they are sown; the liquid which remains is no longer serviceable after forty-eight hours, while the seeds may be sown even after eight or ten days. In Ireland surprising effects were obtained on many sterile soils. In general, however, the best results have been obtained in soils which are not acid or in which the acidity has been corrected with lime, and which also contain plenty of phosphates and of potash.

Hutchinson (International Chemical Congress in London, 1909) obtained good results with cultures of azoto-bacteria even with non-leguminous plants such as tomatoes.

According to W. B. Bottomley (U.S. Pat. 982,569, 1911), a nitragine culture beneficial to other plants besides Leguminosæ may be prepared by mixing azoto-bacteria with *Pseudomonas radicicolo* (the bacterium of leguminous nodules) in the following manner. For the culture liquid 20 grams of mannitol, 1 gram of potassium phosphate, 0·5 gram of magnesium sulphate, and 0·5 gram of calcium carbonate are dissolved in a litre of water. With this are mixed a pure culture of Pseudomonas and, for the nitrogen bacteria, a little well-manured soil. After 7 to 10 days, the brown scum collecting on the surface is used for the preparation of various cultures on agar plates containing a little of the above nutrient solution. Of these new cultures a drop, mixed in distilled water, is transferred to a litre of water containing 15 grams of maltose, 10 grams of mannitol, 1 gram of potassium phosphate, and 0·5 gram of magnesium sulphate. This liquid, kept at 22° to 28° for 36 to 48 hours, gives the mixed bacterial culture and, after dilution, may be used for watering the soil.

a marked improvement. Experiments made by Stoklasa in 1908–1909 by inoculating nitrogen bacteria in cultivated soil planted with oats, beetroot, and potatoes gave good results in regard to quantity and quality. If much calcium carbonate is present in the soil the nitrogen bacteria give advantageous results even with non-leguminous plants.

Other bacteria, called *nitrifying bacteria*, have also been discovered in the soil; these have the property of transforming nitrogenous organic compounds (albuminoids) first into ammoniacal compounds, which are then nitrified by various other bacteria. In the soil the process of bacterial nitration does not commence before all the ammonia or ammonium carbonate has been transformed into nitrites; other ammoniacal salts, on the other hand, do not harm the bacteria, which are sometimes able to transform these directly into nitrates (*see* Biological Purification of Sewage, p. 250).

The nitrifying bacteria need plenty of air and abundant oxygen in the soil,[1] and it appears advantageous therefore to add oxidising substances such as manganese dioxide to the soil; this has been recently tried in the Agricultural School of the University of Tokio, and as is shown by the experiments of Professor Giglioli, the results were generally favourable although not yet decisive. He proposes the addition of 300 to 400 kilos of manganese dioxide per hectare, this being added in such a manner that it penetrates somewhat deeply into the soil. Experiments made in France in 1907 with from 10 to 50 kilos of manganous sulphate per hectare planted with beetroot and potatoes showed hardly any advantage.

(*b*) **ELECTRICAL PROCESS.** The nitrogen problem is to-day rapidly approaching a practical solution, the valuable work already contributed in this direction by well-known scientists during the last few years having encouraged many others to endeavour to solve the question.

Once again the happy union of chemistry and electricity has borne valuable fruit. The solution of certain great problems requires the contribution of several factors, and one of the most important of these, historically speaking, is the time factor; a problem once propounded rarely finds a rational solution without passing through stages.

In 1786 Cavendish showed experimentally that, under the action of electric sparks the oxygen and nitrogen of the air combine, giving, with water, nitric acid, but only since 1900 has this reaction been worked as an industrial process (*see later*, Synthetic Nitric Acid).

(*c*) **CHEMICAL PROCESSES.** The problem of the fixation of atmospheric nitrogen by chemical means has been ingeniously solved in several ways during the last few years, and hundreds of thousands of tons of nitrogen compounds (ammonia, calcium cyanamide,

---

[1] *Theory of fertilisation and bacterial action* (*see also* chapter on Chemical Fertilisers and Superphosphates, Part III of this vol.). The nitrogenous organic matter of animal and vegetable origin found in the soil is transformed by certain bacteria, first into albumoses, then into peptones, and afterwards into amino-acids, which readily (by the action of certain enzymes, *e. g.*, amidases; *see* Vol. II., "Organic Chemistry") yield ammonia, this being oxidised by other bacteria with formation of nitric acid, which is assimilable by plants. If the soil is poorly aerated, owing to deficient working, certain aerobic bacteria withdraw oxygen from the nitrates and cause liberation of nitrogen. This phenomenon of denitration becomes more serious during rainy weather, the air being then expelled from the soil while the water carries away part of the nitrates. These denitrating bacteria develop the more easily if the soil contains much carbohydrate (straw, pentosans, etc., *see* p. 334) derived from excessively new stable manure, which has undergone little fermentation and decomposition. When, however, the soil is well aerated, the nitrate and also the nitrogen are partly fixed by the bacteria themselves to form the proteins of their cellular protoplasm, which, when the organisms die, is utilised, decomposed, and nitrified by other bacteria; even if the proteins are not decomposed immediately, they are not lost, but remain to be used in succeeding seasons. This utilisation and nitrification of the proteins of cells (even woody cells) explain why, in meadows and woodlands used for other crops, nitrogenous fertilisation is not necessary, the plant residues (roots, leaves, etc.) furnishing the nitrifying bacteria with the proteins required for the formation of nitrates.

In order to facilitate the decomposition of the straw of stable manure on the fields, it has been proposed to inoculate the soil with special cultures of the bacteria of such manure. Inoculation of the soil with nitragine gives good results if the soil is poor in *B. radicicola*, and if the nitragine cultures are prepared from the bacteria of nodules from the same leguminous species as is to be grown.

Bacteria act indirectly also on other substances, producing a fertilising effect owing to the generation of large quantities of carbon dioxide (according to Stoklasa, as much as 75 kilos per hectare per day), which readily dissolves insoluble mineral substances, such as carbonates, phosphates, etc. The production of bacterial carbonic acid is favoured by the presence of stable manure and various salts (ammonium sulphate, superphosphate, magnesium sulphate, etc.), and the bacteria assimilate for their own growth phosphoric acid and potash (biological absorption), which are afterwards utilised by the plants.

etc.) are now prepared annually from this source and are utilised in chemical industries and in agriculture (*see* Synthetic Ammonia).

NEW GASES DISCOVERED IN THE ATMOSPHERE

In 1892 Lord Rayleigh, while studying and controlling the densities of the elementary gases by exact methods, constantly found a difference of density between nitrogen separated from the air (1·2572) and nitrogen prepared from ammonia or from nitric acid (1·2507). Rayleigh, although one of the greatest experimental physicists, considered it advisable to continue these studies together with a chemist, Ramsay. In August 1894 these workers communicated to the British Association at Oxford that the high density of atmospheric nitrogen was due to the presence in air of another gas, *argon*. In March 1895 Ramsay, while seeking for other sources of argon and heating uranium minerals, discovered another elementary gas, *helium*, the existence of which had been foreseen for some time on account of its characteristic lines, which were always found in the solar spectrum. More recently Kayser has found small quantities of helium also in the air.

These two new gases are characterised by their indifference towards all other substances; in fact they have not yet been combined with any other element. It was shown that their molecules are monatomic even at the ordinary temperature, whilst before that time free atoms were known only at high temperatures; this fact was deduced by determinations of the relations between their specific heats at constant pressure and at constant volume. The ratio, $\frac{Cp}{Cv}$, was found to be 1·67, as is the case for all monatomic gases, whilst for molecules of di- or polyatomic gases the value is about 1–1·4 (*see* p. 52).

Recently Ramsay, while searching for a new element which should occur in the periodic system between helium and argon, found four other new gaseous elements in air, and succeeded in separating them in an impure state by evaporating 750 c.c. of liquid air to a volume of 70 c.c. He thus discovered *krypton*, of atomic weight 45, with a characteristic spectrum containing a green, a red, and a yellow line similar to the spectrum of the aurora borealis; at the same time he found *xenon*, and finally also *neon*, which has a density of 20 compared with hydrogen, and perhaps constitutes the intermediate member sought for between argon and helium.

ARGON: A, 39.9

Air contains 0·935 per cent. of this gas by volume and atmospheric nitrogen about 1·183 per cent., so that we inspire about 20 litres of it daily.

It is found in certain mineral waters and in the gases of certain springs, and in small quantities together with helium in certain uranium minerals from which it is evolved on heating. Gases occluded in rock salt contain argon, and it has also been found in a meteorite; it is prepared from air in three ways:

(1) Atmospheric nitrogen freed from oxygen and from water vapour is passed over a red-hot magnesium spiral; magnesium nitride is thus formed: $N_2 + Mg_3 = N_2Mg_3$, whilst the argon does not react. This process is repeated many times until the gas no longer diminishes in volume. The nitrogen may be still more rapidly absorbed by means either of lithium or of a red-hot mixture of magnesium and calcium oxide, that is, of finely divided free calcium: $Mg + CaO + Ca$ (the method followed by Ramsay).

In 1908 Fr. Fischer and Ringe prepared argon very easily by passing a current of air (purified and dried with KOH, H_2SO_4, and P_2O_5) over calcium carbide mixed with 10 per cent. of calcium chloride and previously heated *in vacuo* to 800°; in this manner both the nitrogen and the oxygen are absorbed, as the latter transforms the calcium cyanamide into CaO, carbon and cyanamide. In order to free it from the last traces of nitrogen, Fischer and Hähnel (1910) passed this argon several times over red-hot calcium.

(2) Lord Rayleigh mixes atmospheric nitrogen with oxygen in presence of sodium hydroxide solution, and then subjects the mixture to electric sparks for a long time; sodium nitrite is formed and a mixture of argon and oxygen remains, which is passed over red-hot copper in order to remove the oxygen.

In 1785 Cavendish already observed that on treating air in this way all the atmospheric nitrogen is not transformed into sodium nitrite, but that a small quantity of gas remains, which he did not examine, but which he found to have a constant volume, namely, about $\frac{1}{120}$th of the volume of the air.

Argon thus prepared still contains *helium* and *neon*, which are lighter, and krypton and xenon, which are heavier, and it is therefore liquefied by means of liquid air and subjected to fractional distillation.

(3) C. Claude (1910) found that oxygen of 96 per cent. purity, prepared from liquid air, contains up to 3 per cent. of argon. He passed such oxygen through a red-hot copper tube, which fixed the oxygen, and the residual gas through a red-hot iron tube containing powdered magnesium to fix the nitrogen. Traces of hydrogen are then fixed in a red-hot quartz tube charged with copper oxide. In this way 8 to 10 litres of argon may be prepared in two hours; when all the copper is oxidised, it is reduced by means of hydrogen, this requiring 2 to 3 hours.

One litre of argon weighs 1·780 grms., and its density compared with air is 1·376. It is solid at −190° and boils at −185°. Its critical temperature is −121° and its critical pressure 50·6 atmospheres. It is more soluble in water than oxygen (two and a half times more, 100 vols. of water dissolving about 4 vols. of argon at 12°). It therefore accumulates in the gases of rain water and also in the oxygen prepared by Mallet's process (p. 195). By means of its spectrum Crookes was able to distinguish argon clearly from other gases because, apart from various lines in the red and orange and five lines in the green, there is a blue line more intense than that of nitrogen and five other intense and characteristic lines in the violet. The dielectric cohesion of argon is 38 (Moissan and Bouty, 1910).

No chemical combinations of argon are yet known, the yellow solid compound obtained by Berthelot by means of the electric discharge in benzene vapours and argon being not an argon compound.

Even the new attempts of Fr. Fischer and Iliovici and Schröter (1909 and 1910), by passing the electric arc through pure liquid argon from electrodes of various metals at − 189°, led to negative results, as they yield merely metallic powders of various colours, often in the pyrophoric condition. In Germany (1913) use has been made of argon to fill metallic filament electric lamps (even ½-watt), which then last better than those filled with nitrogen.

HELIUM: He, 4

This is an absolutely inactive gas like argon, and is one of the rarest elements on the earth's surface. It is, however, present in abundance in the luminous solar atmosphere and in other stars, together with hydrogen. It was discovered spectroscopically in the solar chromosphere by N. Lockyer in 1867, and he studied it in 1869 together with Frankland, and called it helium.

Palmieri observed it on the earth for the first time in 1882 on studying spectroscopically a stone from Vesuvius.

It was isolated only in March 1895 and defined by means of its complete spectrum by W. Ramsay; before that time only the line D_3 had been known. Ramsay found it while searching for sources and methods of preparation of argon.

When certain rare minerals composed of salts of uranium, yttrium, and thorium—for example, cleveite, uraninite, and monazite—are heated, helium is evolved, together with hydrogen, nitrogen, argon, and carbon dioxide. It is also obtained by treating them with dilute sulphuric acid (1 : 8) or with sodium bisulphate. Kayser found it in minimal quantities in the air, and this observation was confirmed by Ramsay and Travers.

This gas is also found, like argon, in the gases of various springs at Wildbad, at Abano near Padua, and also in the soffioni of Lardarello in the Tuscan marshes.

In 1908 Claude improved the rectifying column of liquid air so as to obtain helium and neon from the residual liquid (Ger. Pat. 239,322). In the gases of a thermal spring of the Cote d'Or, Moureu and Lepape in 1912 found 10 per cent. of helium by volume. The gases of the thermal spring at Wildbad (Wurtemburg) contain 1·56 per cent. of argon and 0·71 per cent. of helium. These springs are exceptionally rich in helium.

The thermal springs of Santenay give annually 18 c.c. of helium and those of Néris 34 c.c., but much larger amounts of helium are present in the gases of certain coal mines, the Frankenolz mines yielding 3650 c.c. per annum, and the gas spring at Kissarmas (Hungary) 4380 c.c. The helium of coal mines bears no quantitative relation to the traces of radium in the coal itself, and must hence have a different origin, as is the case with neon, argon, krypton, and xenon, which are also found in the gas of coal mines and are certainly not derived from the coal.

The molecule of helium is monatomic. Dewar believed that he had succeeded in liquefying it by means of rapid evaporation of liquid hydrogen, but Olszewski showed in 1906 that he had been mistaken. It was liquefied with certainty for the first time by Kamerlingh Onnes on July 10, 1908. It boils at — 268·5° and its critical temperature is perhaps — 268°; when it is rapidly evaporated the temperature is lowered to — 271·8°. The dielectric cohesion (*see above*) is 18. It is employed in the preparation of thermometers for the measurement of low temperatures (*see* L. Rolla, *Annali di chimica applicata*, 1914, II, p. 364).

Helium is the least soluble in water of all known gases. When subjected to powerful electric discharges in a Plücker tube it is absorbed by the platinum electrode, and may be separated from nitrogen in this way; on heating the electrode it is again liberated. The emission spectrum contains five well-marked lines. At a temperature of 900° it diffuses through quartz. The formation of helium from radium and from radio-active substances has already been mentioned on pp. 129 *et seq.* G. Claude (1909) found that in a million litres of air there are 16 litres of neon, 5 litres of helium, and less than 1 litre of hydrogen.

NEON : Ne, 20. This is liquid at a temperature of — 243° and solid at — 252°. Its critical temperature has been calculated to be — 220°. Its spectrum consists of green lines and several orange lines. Collie noticed in 1909 that on passing a bubble of pure dry neon into the evacuated chamber of the Töpler pump this acquires a red luminosity.

With his rectifying column (*see above*) Claude obtained from liquid air as much as 100 litres of neon per day and utilised it for the preparation of vacuum tubes with red luminescence, these giving greater luminosity than those of nitrogen and consuming 0·5 kilowatt instead of 1·7. If the neon is mixed with nitrogen, oxygen, and helium, the gases can be condensed by a prolonged discharge between carbon or metallic electrodes, any traces of argon and hydrogen which remain serving also to produce the Hertzian waves of luminous tubes.

KRYPTON: Kr, 83. This element is liquid at — 152° and solid at — 169°. The green lines of its spectrum are especially characteristic and are also found in the aurora borealis. It is contained in air to the extent of about one part per million.

XENON : X, 130.7. This gas liquefies at — 109° and solidifies at — 140°. Its spectrum contains various characteristic blue lines. It is present in air to the amount of about one part in forty millions.

AMMONIA: NH_3, 17

This compound is found combined with certain acids in the air, in natural waters, and in the soil, but always in small quantities. It is present abundantly as ammonium sulphate in the *soffioni* of Tuscany and occurs as ammonium carbonate in the large guano deposits of Peru.

Ammonia was studied by Priestley, who called it alkaline air; its composition was determined by Berthollet in 1785.

FORMATION. It is formed from hydrogen and nitrogen in small quantities (2 per cent.) by means of the electric discharge, or better in the hot in presence of catalysts (*see later :* Haber's industrial process), but in the presence of moisture, as in the atmosphere, ammonium nitrate is directly obtained: $N_2 + O + 2H_2O = NO_3NH_4$. On the other hand, ammonium nitrite, NO_2NH_4, is obtained whenever combustion occurs in the air and in the electrolysis of aerated water : $N_2 + 2H_2O = NO_2NH_4$. A mixture of NO and H in presence of Pt or of Fe_2O_3 also gives NH_3 on heating.

When certain metals, such as zinc, are dissolved in dilute nitric acid, the nascent hydrogen reduces the nitric acid: $NO_3H + 4H_2 = 3H_2O + NH_3$, and thus ammonium nitrate is obtained together with the zinc nitrate. Salts of nitric acid are also reduced by nascent hydrogen in alkaline solution with production of ammonia.

Its formation from magnesium nitride, N_2Mg_3, is interesting; this substance is obtained by passing N over red-hot Mg, and reacts vigorously with water to form ammonia: $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$.

A large source of ammoniacal salts, and the only one until some time ago, is the putrefaction and decomposition of nitrogenous organic matter or, better still, its dry distillation. It was obtained in this way from urine, camel's dung, etc.

Formerly ammonia was obtained almost exclusively by distilling the gas liquor obtained in the manufacture of illuminating gas, which is prepared by the distillation of coal, but during the last few years it has been manufactured on an industrial scale by various other processes (*see below*).

It is prepared in the laboratory by heating a pasty mixture of solid ammonium chloride and slaked lime in a glass or iron flask on a sand-bath:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$

It is collected over mercury because it is very soluble in water. It is dried by passing it over quicklime (CaO), and not over calcium chloride, with which it combines. It may also be collected by displacement of air in an inverted cylinder, as it is lighter than air.

PHYSICAL PROPERTIES. Ammonia is a colourless gas with an intense, suffocating odour; it has a density of 0·56 (air = 1). At 10° and at a pressure of 6·5 atmos. or at − 40° at the ordinary pressure it is converted into a colourless mobile liquid of sp. gr. 0·623 (water = 1) which boils at − 38·5° (752 mm.) and solidifies at − 85°. Its critical temperature is + 130° and its critical pressure 115 atmos.; the heat of evaporation of liquid ammonia is 297·8 cals. at + 16° and the coefficient of expansion at 15° 0·00225.

One volume of water at 0° dissolves 1146 vols. of ammonia, and at 20° about 739 vols., so that one part by weight of water dissolves 0·526 part by weight of NH_3. A saturated aqueous solution at 15° contains 35 per cent. by weight of NH_3 and has a specific gravity of 0·880. In its aqueous solutions the specific gravity becomes less as the quantity of dissolved ammonia becomes greater, as is seen from the following Table.[1]

Sp. gr. at 15°	Degrees Bé.	Per cent. by weight of NH_3	1 litre of the solution contains grms. of NH_3	Sp. gr. at 15°	Degrees Bé.	Per cent. by weight of NH_3	1 litre of the solution contains grms. of NH_3
0·998	10·5	0·45	4·5	0·938	19·5	16·22	152·1
0·994	10·9	1·37	13·6	0·934	20·3	17·42	162·7
0·990	11·5	2·31	22·9	0·930	21·1	18·64	173·4
0·986	12·0	3·30	32·5	0·926	21·8	19·87	184·2
0·982	12·5	4·30	42·2	0·922	22·4	21·12	194·7
0·978	13·0	5·30	51·8	0·918	23·0	22·39	205·6
0·974	13·9	6·30	61·4	0·914	23·6	23·68	216·3
0·970	14·5	7·31	70·9	0·910	24·4	24·99	217·4
0·966	15·0	8·33	80·5	0·906	25·0	26·31	238·3
0·962	15·7	9·35	89·9	0·902	25·7	27·65	249·4
0·958	16·3	10·47	100·3	0·898	26·5	29·01	260·5
0·954	17·0	11·60	110·7	0·894	27·4	30·37	271·5
0·950	17·7	12·74	121·0	0·890	28·0	31·75	282·6
0·946	18·3	13·88	131·3	0·886	28·7	33·25	294·6
0·942	19·0	15·04	141·7	0·882	29·5	34·95	308·3

---

[1] The density determined at a temperature higher or lower than 15° is corrected to 15° by increasing or diminishing it by 0·00020 for each degree for the density 0·994 and by coefficients increasing to 0·00040 for the density 0·938 and to 0·00060 for the density 0·890. Thus, suppose a solution shows the density 0·900 at 13°; the coefficient interpolated between 0·890 and 0·938 is 0·00057 and the true density at 15° has the value 0·900 − (15–13) 0·00057 = 0·8989.

On heating, all the NH_3 is evolved from its aqueous solutions, and pure water remains. When ammonia dissolves in water much heat is evolved, and much is absorbed when it is evaporated or liberated, and these properties were utilised practically for the first time by Carré for the preparation of artificial ice by cooling water. When a solution of NH_3 which is kept saturated is cooled to − 79°, thin crystals of NH_3, H_2O, containing 48·6 per cent. of NH_3, separate, together with thick crystals of $(NH_3)_2, H_2O$, containing 65·4 per cent. of NH_3. A solution containing 33 per cent. of NH_3 becomes very dense and viscous at − 100°. Methyl alcohol dissolves 29·3 per cent. of NH_3 at 0° and 20·8 per cent. at 17°, and ethyl alcohol, 19·7 per cent. at 0° and 12·6 per cent. at 17°.

CHEMICAL PROPERTIES. On passing electric sparks through ammonia for a long time, or on heating it to above 500°, it decomposes to the extent of 98 per cent.

Ammonia does not burn in the air, but burns in oxygen with a yellowish flame, yielding free nitrogen, nitric oxide, and ammonium nitrite. When magnesium is heated in a current of NH_3 it catches fire, forming hydrogen and magnesium nitride: $3Mg + 2NH_3 = Mg_3N_2 + 3H_2$; potassium acts similarly: $3K + NH_3 = NK_3 + 3H$.

If a current of chlorine is passed into a flask full of ammonia the chlorine catches fire and continues to burn, forming white vapours of ammonium chloride together with nitrogen: $NH_3 + 3Cl = 3HCl + N$, and $3NH_3 + 3HCl = 3NH_4Cl$.

In aqueous solution or in the state of gas it has always a strongly basic action (*see* explanation in Part III in chapter on Ammonium) and neutralises acids forming salts analogous to those of the alkali elements, potassium and sodium:

$2NH_3 + SO_4H_2 = SO_2(NH_4)_2$ analogous to SO_4K_2 and SO_4Na_2.
$NH_3 + HCl = NH_4Cl$,, ,, KCl ,, $NaCl$, etc.

Thus the group NH_4, which is called *ammonium*, may be considered almost as an element, and in its behaviour it is similar to the alkali metals and even forms an amalgam with mercury in the same way as these do (*see* Part III). Its salts are called ammonium salts and their ammonia may be eliminated by the action of more energetic bases such as lime, sodium hydroxide, etc.:

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

Traces of ammonia are detected by means of Nessler's reagent (*see* Analysis of Water, p. 234, *and* Mercuric iodide).

The heat of formation of NH_3 from its elements (corrected by Haber in 1914) is 13,200 cals. at the temperature of formation (659°), and it develops a further 31·1 Kj. (7433 cals.) on dissolving in water.

The constitution of ammonia may be determined from its analysis, that is to say, from its percentage composition, from the density of the gas, and directly by the electrolytic decomposition of aqueous ammonia solution in a Hofmann voltameter, the ammonia solution being saturated with sodium chloride, which renders it more conductive; at the negative pole 3 vols. of hydrogen are separated, and at the positive pole 1 vol. of nitrogen, so that the ammonia decomposes forming 3 vols. of H and 1 of N. On passing the electric spark through a definite volume of ammonia for some time, it is completely decomposed into N and H, forming a volume double that of the NH_3: 2 vols. NH_3 = 1 vol. N_2 + 3 vols. H_2.

INDUSTRIAL PREPARATION OF AMMONIA

The only natural salt utilised for this purpose is the ammonium sulphide of the soffioni of Tuscany. From four soffioni 1500 kilos of ammonium sulphate have been extracted in twenty-four hours, together with 150 kilos of boric acid, 1750 kilos of magnesium sulphate, and 750 kilos of iron and magnesium sulphates.

A small quantity of ammonia is also prepared from beet-sugar residues (molasses), these containing nitrogenous organic substances (*betaine* and *aspartic acid*), which yield ammonia and trimethylamine on dry distillation. The latter compound is in turn decomposed by HCl forming ammonium chloride and methyl chloride, CH_3Cl. Ammonia is also obtained from putrefied urine by Figuera's process (at Chicago, for example, the putrefied urine from the large slaughter-houses for the pigs is utilised).[1]

We must also mention the industrial preparation of NH_3 from atmospheric nitrogen by means of calcium cyanamide and steam or hot water under pressure (*see* p. 371) and also by the catalytic process from its elements (Ostwald and also the Badische Anilin und Soda-fabrik; Fr. Pat. 406,943 of 1909).

I. AMMONIA FROM ILLUMINATING GAS. Almost the whole of the ammonia which is prepared to-day is derived from the gas water of gas-works, and from the distillation of coal during the preparation of metallurgical coke (*see* Vol. II., " Organic Chemistry ").[2]

To utilise the ammonia from small quantities of ammonia liquor, this is sometimes neutralised with sulphuric acid and evaporated in wrought-iron pans by means of hot regenerator or flue gases. This procedure yields a highly impure crude ammonium sulphate which is of low value, although it costs a great deal, 90 per cent. of the water of the solution having to be evaporated.

---

[1] During the fermentation of urine the urea which it contains is transformed into ammonium carbonate, $CO(NH_2)_2 + 2H_2O = CO_3(NH_4)_2$, and this is readily decomposed on heating, forming $CO_2 + 2NH_3 + H_2O$. Every adult person produces 30 grms. of urea daily, corresponding with an annual production of more than 20 kilos of ammonium sulphate, so that the urine of the inhabitants of Milan would suffice for the annual production of about 14,000 tons of ammonium sulphate.

[2] Of the nitrogen contained in coal (up to 1½ per cent.) only 15–20 per cent. is transformed into NH_3 and 35 per cent. is evolved as free nitrogen, because in the retort in which the coal is distilled a temperature of 1200° is reached whilst ammonia commences to dissociate into H and N even at 500°; 48 per cent. of the nitrogen of the coal remains in the coke. If NH_3 had a higher value it would be possible to increase the yield during gas manufacture by distilling the carbon in presence of steam, which carries off the NH_3 and lowers the temperature.

How the nitrogen of coal originates is not very clear and it is usually considered to be derived from the proteins and other nitrogenous substances of the plants from which the coal was formed (*see later :* chapter on Coal). When the coal is distilled in retorts, that part of the nitrogen not obtained as ammonia in the wash-water is found in the tar as pyridine, pyrrole, quinoline bases, etc., while part is lost as free nitrogen and some remains in the coke, probably as cyanides, nitrides, etc., which yield ammonia to some extent when treated with steam. An attempt has been made to increase the yield of ammonia by mixing lime with the coal, but in general this procedure is of little avail (Cooper, Eng. Pat. 5713, 1882), although with certain Saxon coals (containing large amounts of chlorides in the ash) it results in the conversion of as much as 84 per cent. of the nitrogen into ammonia. By gasification of the coal or coke in presence of steam the nitrogen is better utilised.

According to the quality of the coal the ammoniacal liquor from gas-works contains from 12 to 35 grms. of NH_3 per litre (density 3–4° Bé.), partly as volatile compounds : hydroxide (trace), carbonate, sulphide and cyanides, and partly as fixed compounds : chloride, sulphate, sulphites, thiosulphate, ferrocyanide, and thiocyanate. English coals and German ones of the Saar and Ruhr districts give ammonia liquors with a large preponderance of volatile ammonia (80–90 per cent.), whilst those from Saxon coals (Zwickau) contain about 90 per cent. of fixed ammonia. The principal components of these waters are as follows :

	English and German (Ruhr and Saar) Coals.	German Coals (Zwickau)
Total ammonia, grams per litre . .	15–18	9–12
Ammonium thiosulphate ,, . .	2–5	1–1·6
,, sulphide ,, . .	3·4–6·3	0·3–0·7
,, carbonate ,, . .	30–33	4·5–7·7
,, bicarbonate ,, . .	2–3	1–1·5
,, sulphate ,, . .	1–2	0·4–0·9
,, chloride ,, . .	3–4	17–30·5

The ammonia liquors are kept in cemented brickwork tanks with a mortar of asphalte, or better in wrought-iron tanks in which the tar completely separates, to be removed below.

If the price of sulphuric acid is high, ammonium sulphate may be obtained (Warth, 1906) by heating the ammonia liquor with gypsum, about 17 per cent. of the ammonia then distilling, while the remainder gives ammonium sulphate solution, which is filtered and concentrated.

The ammonia is usually liberated by distilling the ammoniacal liquors with lime (to fix the CO_2 and H_2S of the sulphides and carbonates) and the ammonia is absorbed by strong sulphuric acid (50–60° Bé.). Crystallised ammonium sulphate is thus directly obtained and is easy to handle and transport. This distillation requires far less fuel than complete evaporation of the ammonia liquor neutralised with sulphuric acid (*see above*).

A very simple apparatus used in many works is that of Lunge (Fig. 136). The cold ammoniacal liquor passes into the reservoir *d*, and there cools the coil which carries the steam (which condenses) and ammonia from the pan, *a*, into which the ammoniacal liquor passes through the tube *e* from the vessel *d*; *b* is a stirrer for preventing the lime from settling on the bottom, and *g* a valve from which the exhausted liquor is discharged through the tube *f*. When the gas liquor in *d* is sufficiently heated it evolves vapours which escape through the small curved tube and join those proceeding from the boiler; *k* is a washing vessel for the ammoniacal vapours, which are then absorbed by strong sulphuric acid in the vessel *l*, lined with lead. The sulphuric acid passes into this saturator from the reservoir *O*, through the syphon, *P*; the crystals of ammonium sulphate are collected with a ladle into a perforated bucket, *S*, which is lifted by means of a counterpoise. The evil-smelling gases which are not absorbed by the strong sulphuric acid contain hydrogen sulphide and cyanogen compounds. These gases cannot be led directly up the chimney because they would cause annoyance in the neighbourhood; it is therefore preferable to burn them by passing them below the hearth of a furnace containing red-hot coal, or the cyanogen compounds which they contain may be utilised by passing them through suitable solutions (*see* Vol. II., "Organic Chemistry," Illuminating Gas) and the hydrogen sulphide afterwards either utilised in a Claus kiln for the recovery of the sulphur (*see* Part III, Leblanc Soda), or absorbed by iron oxide.

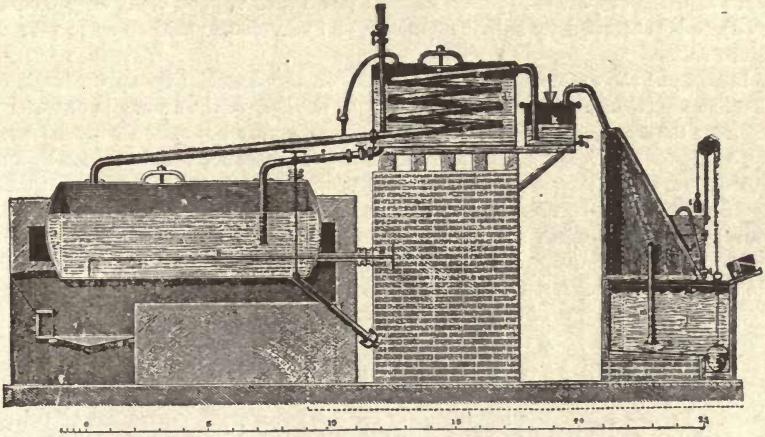


FIG. 136.

The Lunge apparatus is now little used, its only advantage being its great simplicity; in any case it would be more convenient to use a larger coil, *c*, easily freed from deposited ammonium carbonate.

The apparatus in most common use in practice since 1885 are those (proposed by Laming in 1840) based on the principle of the Savalle rectifying column (as used in spirit distilleries). Numerous different forms and modifications have been proposed, the principal patents being: Ger. Pats. 124,978, 140,824, 150,228, 153,475, 169,444, 188,814, 194,567, 200,592, 204,858, 205,773, and 217,680.

The modern forms are continuous and admit of large outputs (even more than 100 cu. metres in 24 hours) with a minimum of machinery and with maximal yields. Their rational working is based on the following considerations: the ammonia of ammonia liquors is all combined, and to liberate it from the various salts would necessitate its treatment when boiling with an energetic base. The lime used for this purpose costs little, but in some cases large amounts (up to 50 kilos per cu. metre) would be required, and bulky, inconvenient deposits of calcium carbonate and sulphate mixed with sulphide, cyanide, etc., would be formed with continual danger of obstruction in the apparatus. On the other hand, most of the ammonia in these liquors is in the form of salts, which readily dissociate in the hot (carbonate and sulphide). It is best, therefore, first to heat the liquor in a suitable apparatus (as suggested by Hill in 1868) or dissociation column at about 93–95°, because at such temperature the sulphides and carbonates are almost completely dissociated into CO_2, H_2S, and NH_3 (the dissociation begins at 50°), but the free ammonia remains dissolved in the water, whereas the CO_2 and H_2S are almost completely evolved (80–90 per cent. of the CO_2 and 60–70 per cent. of the H_2S). One-third of the amount of lime that would be originally required is then often sufficient to decompose the fixed salts (sulphates, etc.) remaining with the free ammonia.[1] The ammonia liberated in the decomposition column cannot be mixed with the gas from the dissociation apparatus, as it would recombine with the CO_2, forming bulky, crystalline ammonium carbonate, which would obstruct tubes and apparatus. Consequently this ammonia, mixed with water vapour, is passed into a more or less complex cooler according to whether all the ammonia is required in aqueous solution or part is required gaseous (the water vapour being only incompletely condensed), to be absorbed by sulphuric, nitric, or hydrochloric acid so as to give directly ammonium salts.

The heating of the ammonia liquor to 93–95° in the dissociation apparatus is effected by indirect steam (so as not to dilute the liquor), or the heat of the ammonia or water vapour escaping from the decomposition column and that of the very hot exhaust waters discharged from the column is recovered. The quantity of lime to be added is determined by analysing from time to time both the ammoniacal water entering the top of the decomposition column and the milk of lime to be used (1 part by weight of NH_3 requires 1·7 parts of CaO, calculated pure), about one-tenth more than the calculated amount being always used; the exhausted water flowing from the decomposition column is examined at frequent intervals to make sure that it does not contain more than 0·005 per cent. of NH_3 (fixed).

Among the many forms of apparatus which are used (Beckton, Mallet, Garcis, Solvay, Feldmann, Koppers, etc.) one which yields very good results is that of Grüneberg and Blum, which completely exhausts the ammoniacal liquor until only one part of NH_2 remains per 10,000 parts of water, and is capable of treating 30 to 50 cu. metres of liquor per twenty-four hours. In this apparatus the dissociation column for the separation of the CO_2 and H_2S has not yet been applied.[2]

The ammoniacal liquor passes through the tube *a* into the pre-heater, *B* (Fig. 137), and from there through the tube *b* into the rectifying column, *A*, where it descends and encounters the hot vapours which pass up from below. At the bottom of the column the liquid passes through the tube *e* into the vessel *F*, containing milk of lime, which decomposes the fixed ammoniacal salts and liberates ammonia. When the liquid in *F* rises to the level of the tube *f* it passes into the vessel *g*, and when this is full it overflows into *h*, and over the circular plates, which are arranged in steps. In this way the quantity of liquor which covers the first step gradually expands over wider and wider surfaces as it descends because the circumference of the circular steps increases, and thus the layer of liquid gradually becomes thinner. In the chamber surrounding the steps there is a series of concentric vertical diaphragms, *i*, which pass down almost to the level of the steps, forcing a current of steam proceeding from the boiler, *G*, and the tube *d*, to play on the liquid surface as it passes down the steps in such a way that even the last traces of ammonia are completely removed. The exhausted water is discharged by the hydraulic syphon, *k*; the steam and ammonia ascend through the tubes *m* and are forced by the tubes *n* to pass through

---

[1] About 8 kilos of quicklime is used per cu. metre of ammonia and is slaked so as to give a dense paste, which is passed through a sieve with a mesh of 1 mm. and allowed to settle, the water separating being then removed. With the remaining paste milk of lime of about 10° Bé. is prepared, this being pumped into the column apparatus (the milk of lime may also be prepared as indicated in Ger. Pats. 164,723, 165,098, and 226,109).

[2] In modern column apparatus, the treatment of 1 cu. metre of ammoniacal liquor requires a consumption of about 250–300 kilos of steam (*i. e.*, about 36–42 kilos of coal).

the milk of lime in *F*, being thus further enriched with ammonia (in *F* the steam pressure is still 0·1–0·3 atmos. per sq. cm.), and then pass up the rectifying column where the water is largely separated. The ammonia, on the other hand, issues from the top of the column by the tube *p* and passes into the saturator, *D*, containing H_2SO_4. The moist ammonia passes into sulphuric acid of 50–60° Bé. During normal working the acid in the saturator is maintained between 32° and 35° Bé., the acid which is removed in the form of crystallised ammonium sulphate being replaced by fresh quantities of acid of 60° Bé. The acid in which the crystals of ammonium sulphate float passes along a tube provided with a steam injector into a leaden box with an inclined bottom, where the crystals are deposited; these are then centrifuged, whilst the decanted acid is returned to the saturator. The evil-smelling gases (H_2S, etc.) which collect in *q* are made to pass through a second sulphuric acid saturator, if they still contain a little ammonia, and then pass through the tubes *r* and *s* and into a furnace, where they are burnt, or the cyanogen and sulphur compounds are utilised as described above or are absorbed by natural ferric hydroxide, as in the purification of illuminating gas (*see* Vol. II., "Organic Chemistry"). The pump, *G*, is used for passing the milk of lime into *F*.

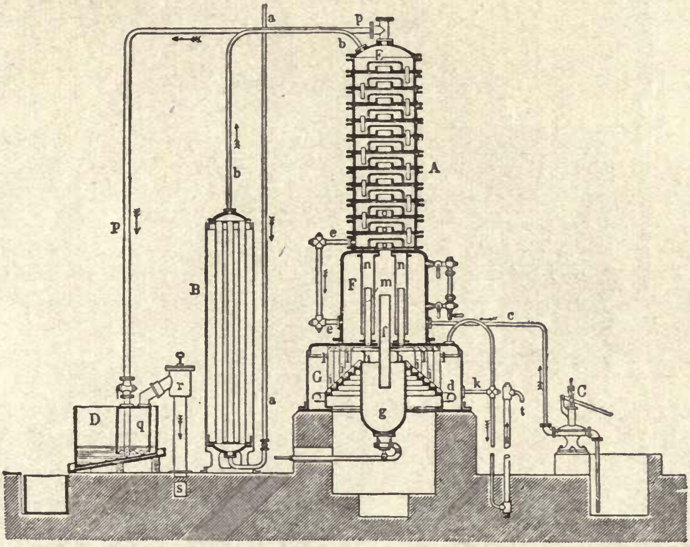


Fig. 137.

The whole of the apparatus, the pipes and utensils, used in the manufacture of ammonia must be made of cast- or wrought-iron. There must be no copper or brass parts because these are strongly attacked by NH_3; at certain points lead is also used.

During recent years use has been made of the Kubierschky column (Ger. Pat. 194,567), which allows the vapours to be circulated as a counter-current to the liquid from which they are derived, the friction being reduced to a minimum compared with that of ordinary rectifying columns. This column, which has been applied in various industries, is described in Vol. II., "Organic Chemistry."

In order to give some idea of the dissociation columns for the separation of CO_2 and H_2S, an illustration is given here of the Solvay apparatus (Ger. Pat. 49,500), from which all others have been derived. The ammoniacal liquor, from a tank, *R* (Fig. 138), above, enters the bottom of the third compartment, *g*, of the column *C*, being fed into a coil, *i*, which carries it up through two other compartments and transfers it through the tube *o* to the washer, *W*. Thence it is discharged by the tube *p*, which carries it to the fifth (uppermost) chamber, b_4, of the dissociation column, from which it descends by the tube f_4 to the fourth chamber, b_3, then by f_3 to b_2, by f_2 to b_1, and finally by f_1 to *b*. It next passes, almost free from CO_2 and H_2S, along the tubes *z* and *v* to the top of the decomposition column, *A*, only the upper part of which is shown in the figure.

The ammonia and water vapour, issuing very hot from the top of the column *A* through the tube *t*, by means of the serpentine tube cc_4 and ww_4 rise through and heat the five chambers b–b_4, so that the temperature in the ammonia water in b is brought to 97–98° and that in b_4 to 93°. The volatile ammonium salts are thus dissociated and the CO_2 and H_2S rise and in each chamber bubble through the ammonia liquor by means of the tubes d_1–d_4, which are furnished with hydraulically sealed caps, e_1–e_4, and give communication between each chamber and the one above. The CO_2 and H_2S escape by the tube *m* and pass into the washer, *W*, where any traces of ammonia are withdrawn, and are then either burnt or utilised as described later. If a little ammonia water condenses from the hot ammonia and water vapour in the pipe $w - w_4$, it is carried into the column *A* by means of the tubes *Z*. From w_4 the moist ammonia vapours pass into the chamber *g*, where they condense in contact with the cold coils *i*, inside which the crude ammonia water flows; the condensed liquid falls successively into the two chambers below and collects in the tank, *X*, as more or less concentrated, pure aqueous ammonia. If ammonium sulphate is required the arrangement of these three chambers is altered so as to condense mainly the water, the ammonia remaining being then fixed by sulphuric acid in a suitable neutraliser.

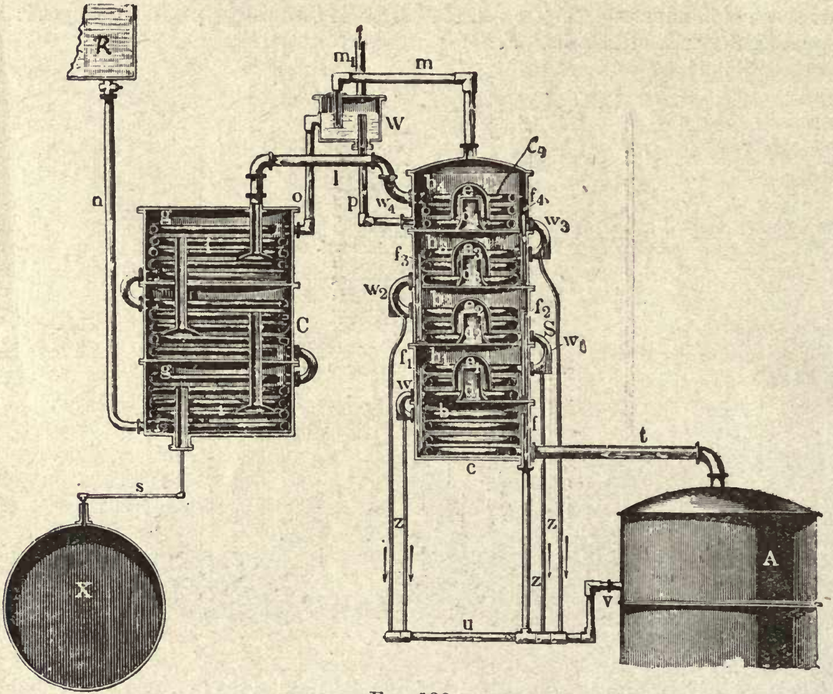


Fig. 138.

When aqueous ammonia is desired instead of ammonium sulphate, it suffices to replace the sulphuric acid of the absorption tank by water which is kept very cold. In this way the volatile salts (ammonium carbonate and sulphide) also are condensed, and to obtain pure ammonia it is best at the beginning to add milk of lime to the ammoniacal water which is distilled, the CO_2 and H_2S being thus retained. Before absorption, the gaseous ammonia evolved at the top of the rectifying tower is passed through either a paste of lime and ferric hydroxide or 10 per cent. caustic soda solution. The water increases in volume by 50 per cent. or even 75 per cent. when a concentration of 25–30 per cent. NH_3 is reached.

Pure ammonia is obtained according to Frerichs (U.S. Pat. 905,415 of December 1908) by first heating commercial ammonium sulphate to 200° to decompose organic impurities and then to 350–400°, at which temperature NH_3 and $(NH_4)_2S_2O_7$ are formed.

Crude commercial ammonia has a yellow colour due to sulphides, pyridine compounds, and tarry matter, and must be purified by distilling it in presence of a little potassium permanganate.

II. AMMONIA FROM OTHER SOURCES. In certain cases NH_3 is also obtained from animal refuse, such as solid excrement, horns, hides, nails, tendons, cuttings from hides, woollen waste, corpses of animals, etc. These substances contain 12 to 18 per cent. of nitrogen and on dry distillation yield an *animal oil* rich in organic bases, such as pyridine, picoline, lutidine, and collidine, together with cyanides, ammonium sulphide, and more particularly ammonium carbonate. Such substances are treated in iron retorts similar to those used in the manufacture of lighting gas.

III. AMMONIA FROM THE NITROGEN OF FUELS. Various investigations (1890–1907) show that the quantity of ammonia obtainable from the nitrogen of coal depends, not on the absolute amount of nitrogen present, but more especially on the way it is combined and on the conditions under which the fuel is gasified. Thus, almost twice as much ammonia is obtained with vertical as with horizontal retorts, since in the former case the gas traverses a deeper layer of the fuel and reaches heated surfaces less easily. L. Mond (Eng. Pat. 12,440, 1893) obtained as much as 3 per cent. of ammonium sulphate from coal in gas producers by injecting into these a current of superheated steam together with a little air at 150°. By this process more than 1,000,000 tons of coal are gasified annually (the first Mond plant was erected at Northwich in 1895). In Germany, owing to the initiative of Frank and Caro, a Mond gas plant was erected at Mont Cenis in Sodingen, 4 kilos of ammonium sulphate and 350 cu. metres of gas with a mean calorific value of 1150 cals. being obtained from 100 kilos of coal (75 per cent. of the nitrogen present is utilised).

Caro (Ger. Pat. 198,295 of 1905) applied the Mond process to the utilisation of the waste coal obtained in large accumulations from the sieving and washing of the coal. This waste contains up to 60 per cent. of ash (mineral matter), but requires a large excess of steam (1 ton per ton of coal) to yield gas of 1000 cals. per cu. metre and 25 kilos of ammonium sulphate (if the coal contains 1·5 per cent. N); to obtain better results it is convenient to mix the waste coal with good coal so as to diminish the percentage of ash.

According to a patent of Ireland and Suyden of London (Ger. Pats. 175,401 of 1903 and 176,606 and 180,141 of 1905), ammonia is formed from atmospheric nitrogen by passing into a cylinder filled with peat and heated to 400° a current of hot air and of atomised water in such a manner as to maintain a temperature of 400°, the reaction being exothermic. The quantity of air is regulated in such a manner as to burn the peat in four to six hours. The gases then pass into a tower filled with pebbles or charcoal in order to retain dust and tar, and then into a second tower, similar to the preceding one, but through which a hot solution of soda or of lime passes in order to absorb the acetic acid; they are finally passed through two other towers, down which hot sulphuric acid is passed to absorb the ammonia. 12·5 kilos of crystallised ammonium sulphate are obtained from 300 kilos of peat.[1]

Frank and Caro showed that when peat is used, especially if moist, the ammonia formed is derived from the nitrogen in the peat itself, and that the yield in ammonia is improved if the decomposition of the peat takes place at

---

[1] In an almost identical patent (Ger. Pat. 146,712, 1902; Eng. Pat. 8358 of 1906) Woltereck starts from the fact that on passing H and N over almost red-hot reduced iron ammonia is formed, and he replaces the necessary hydrogen by moist peat containing 65 to 75 per cent. of water, whilst by other processes dry peat is used. At Carnlong, in Ireland, a similar plant gives a yield of 5 to 7 per cent. of ammonium sulphate calculated on the dry peat, 1 per cent. of acetic acid, and 3½ to 6½ per cent. of tar and paraffin wax. The cost of production of the ammonium sulphate is £4 16*s*. to £6 per ton. It appears, however, that the ammonia is formed from the nitrogen in the peat of which about 60 to 85 per cent. is transformed into ammonia (dry peat contains 2 to 2½ per cent. of nitrogen). In this process combustible power gas is not obtained as is the case in the processes of Mond and of Frank and Caro, so that it appears that in practice it cannot be very remunerative. In 1884 L. Mond and in 1911 Caro showed that in analogous processes the ammonia formed is derived, not from the atmospheric nitrogen, but from the combined nitrogen of the gasified material; Woltereck (1911) contests this statement.

above 250°. They therefore lagged the producers well to prevent dispersion of heat and injected the current of air and superheated steam not only below the producers, but also at several points of its height. Thus instead of utilising only 15–20 per cent. of the nitrogen of the peat, they were able by using moist peat (40–60 per cent. of moisture) to transform as much as 90 per cent. of the nitrogen into ammonia.[1]

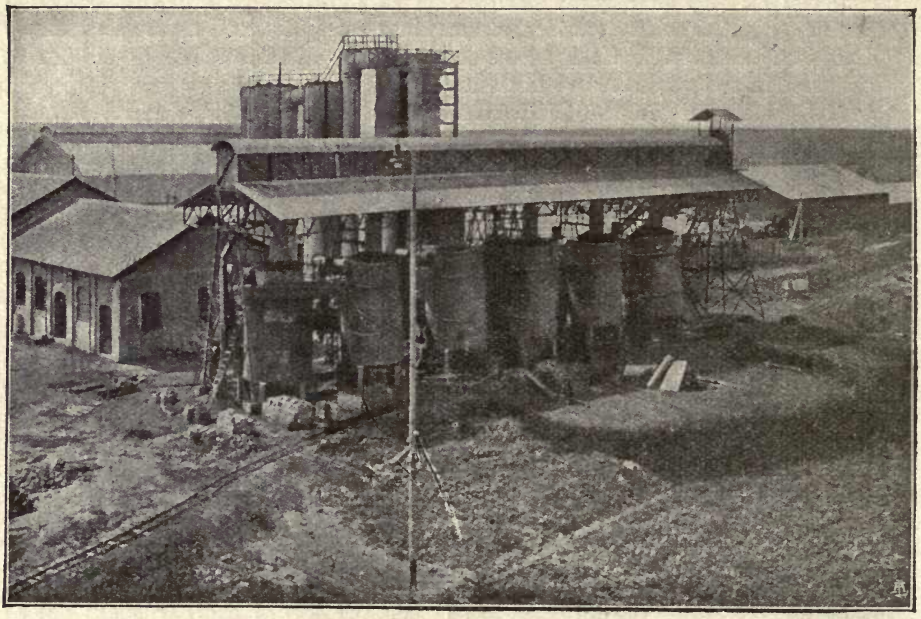


FIG. 139.—Battery of six gas producers for utilising peat at Codigoro.

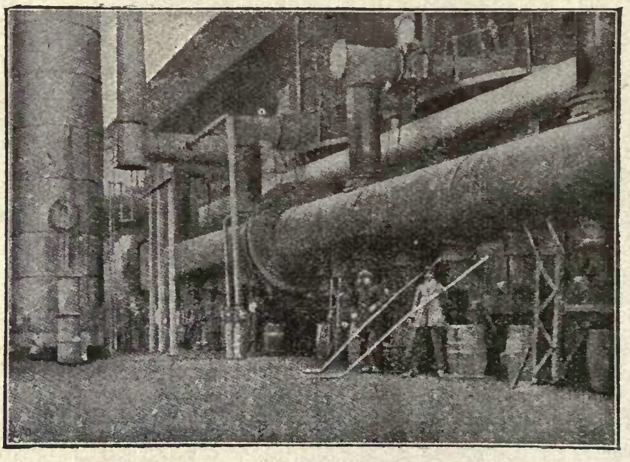


FIG. 140.—Collecting tube of the six Mond gas-producers at Codigoro.

---

[1] In an industrial test made in 1908 on 350 tons of peat containing (dry) 3·7 per cent. of ash, 1·2 N, 51·3 C, 4·6 H, and 39·2 O, Caro from each ton of dry material obtained 2800 cu. metres of gas (almost free from tar). This was composed of 18 per cent. of CO_2, 10 per cent. of CO, 24 per cent. of H, 3 per cent. of methane, 44 per cent. of nitrogen, and traces of oxygen, and had a calorific power of 1400 Cals. per cu. metre. On distilling peat containing 65–70 per cent. of moisture the volume of gas was increased, but its calorific power diminished, although it could still be utilised in internal-combustion engines (in the same way as blast-furnace gases, which are still poorer) and also for heating purposes. The first gas produces one effective h.p.-hour of energy per 2·4

The **MOND PRODUCER** is shown diagrammatically in Fig. 141. It consists of an iron-bound cupola furnace, lined inside with refractory material. The hearth has a basket grate, *a*, which is prolonged below in the form of a sheet-metal cone dipping into the water of the pan underneath, *b*. The charge of peat is introduced by means of the hopper, *d*, the cap, *g*, being displaced. Peat is added until it covers the lower mouth of the bell, *c*; about 400–500 kilos are added every half-hour (about 20 tons per 24 hours). The ash falling into the pan of water is removed from time to time with shovels, so that the working is continuous. The air and steam are fed from above peripherally into the hot space, *e*, round the furnace and pass below the hearth. The new peat added each time in the bell, *c*, gradually undergoes in this zone—which is already hot—incipient distillation, and the gas evolved, which is rich in tar, before it reaches the exit tube, *f*, must pass below the lower edge of the bell, *c*, where the temperature is higher; the tar vapours thus burn without producing the tarry deposits and obstructions experienced in the older gas-producers used for bituminous coal refuse. The hot gases which reach the tube *f* pass into the inner tube of the double surface cooler, *B*, where they meet as a counter-current the cold air injected by a fan; the air is thus heated and then passes, as already stated, through the outer space of the furnace before reaching the hearth, *a*. The gases of the producer, *A* (Fig. 143), after traversing the battery of atmospheric coolers, *B* (where a very

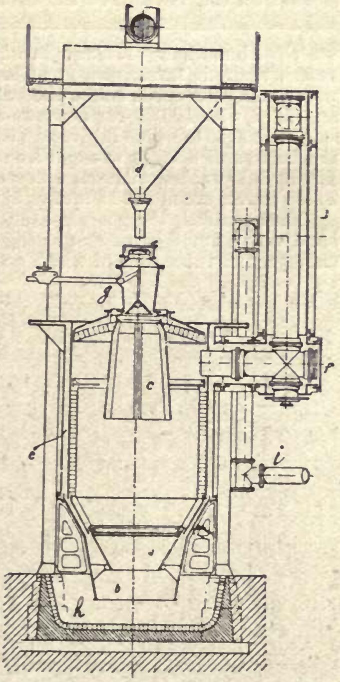


FIG. 141.

---

cu. metres of gas, and therefore 1160 h.p.-hours per ton of dry peat per hour, that is, per 2 tons of peat containing 50 per cent. of moisture. The gases which escape from the gas-engine have a temperature of 500°, and may be used for the production in boilers of steam which is used in the producers and to work the pumps, etc. In this way one may calculate a net yield of 1000 h.p. utilisable in other ways. Furthermore, 40 kilos of ammonium sulphate are obtained, so that 77 per cent. of the nitrogen contained in the peat is utilised. Peat containing 2·8 per cent. of nitrogen (on the dried matter) gave up to 110 kilos of ammonium sulphate per 1000 kilos of dry matter.

In the important peat-beds of Tuscany (Orentano) in 1909 a plant was erected for utilisation of dry peat containing 1·5 per cent. of nitrogen; about 20,000 tons of the peat gave 210 tons of ammonium sulphate, 45,000,000 cu. metres of gas, and about 2000 continuous h.p. hours, that is, about 3½ cu. metres of gas per h.p.-hour; 70 tons of peat are worked per day, costing about 3*s.* 2*d.* per ton at the works, by a plant which costs about £12,000 and is very remunerative. After the plant had worked for some years in the face of great difficulties, especially as regards the furnaces and the excessive cost of drying and transporting the peat and partly the rather low proportion of nitrogen in the peat, the operations were suspended and the company transformed into a larger one for treating on the spot Codigoro (Province of Ferrara) peat, which contains 2–5 per cent. N on the dry matter. The new company has at its disposal about 1200 hectares of peat with a mean thickness of 50 cm., the lower parts being fibrous and the upper powdery. Whereas in other countries failure has been caused by the expense of drying the peat in the sun (first transport on to large surfaces, spreading, turning, heaping, then transport to the store and afterwards transport to the works, etc.), at Codigoro the peat extracted is dried daily on sheets placed on trolleys in large drying galleries, a current of hot gases produced by the combustion of a good part of the gas from the peat gas-producers serving to reduce the moisture from 58 per cent. to 30 per cent. Before drying, the peat is rendered homogeneous by being passed through two mixers in turn, the fibrous part being comminuted and mixed well with the powder. In 1913–1914 six gas-producers, each capable of gasifying 30 tons of peat per twenty-four hours (*see* Fig. 139), were constructed at Codigoro. Treatment of 150 tons of peat in twenty-four hours yielded 270,000 cu. metres of gas with a calorific value of 1400 cals. (10 per cent. CO, 20 per cent. CO_2, 25 per cent. H, 5 per cent. CH_4), about 30 per cent. of ash remaining. The cost of excavation, transport, mixing, drying, and transport to the gas-producer is calculated at 2*s.* 5*d.* per ton and 3 cu. metres of moist peat are required to give in the factory 1 ton of peat calculated anhydrous. In order to obtain the maximum yields of ammonia and Mond gas, the peat in a certain zone of the producer is ignited and traversed by a current of hot air saturated with water vapour. The Mond gas obtained is passed into a large wrought-iron collecting tube capable of dealing with 12,000 cu. metres per hour (Fig. 140), and is washed in a little tar and dust are deposited, these being easily removable from suitable chambers situate on the bottom of the cooling tubes), pass into the washer, *C*, where two rapidly

---

vessel with mechanical stirrers in which part of the tar is deposited; it then passes into another vessel, where it traverses a great length of tubing in order to separate much of the suspended water, and afterwards enters the bottom of a leaden tower supported by a woodwork structure and filled with 50,000 earthenware rings. The gas passing up the tower meets a fine spray of sulphuric acid to which it gives up its ammonia, and on escaping at the top descends in a tube to the bottom of a large wrought-iron tower, where it is partially cooled by a cold water spray. Finally it is washed with water in a third tower, in which the washing and cooling are completed. These towers are about 18 metres high and 3 metres in diameter (Fig. 140).

Thus purified, the gas passes into another collecting tube which communicates on the one hand with a small gasometer acting as a small reserve, and on the other is distributed into two underground tubes, one of which goes to jets, where it is burnt to heat the peat dryers, and the other to the burners under the steam boilers. Before it could be used for gas engines, the gas would require further washing and drying.

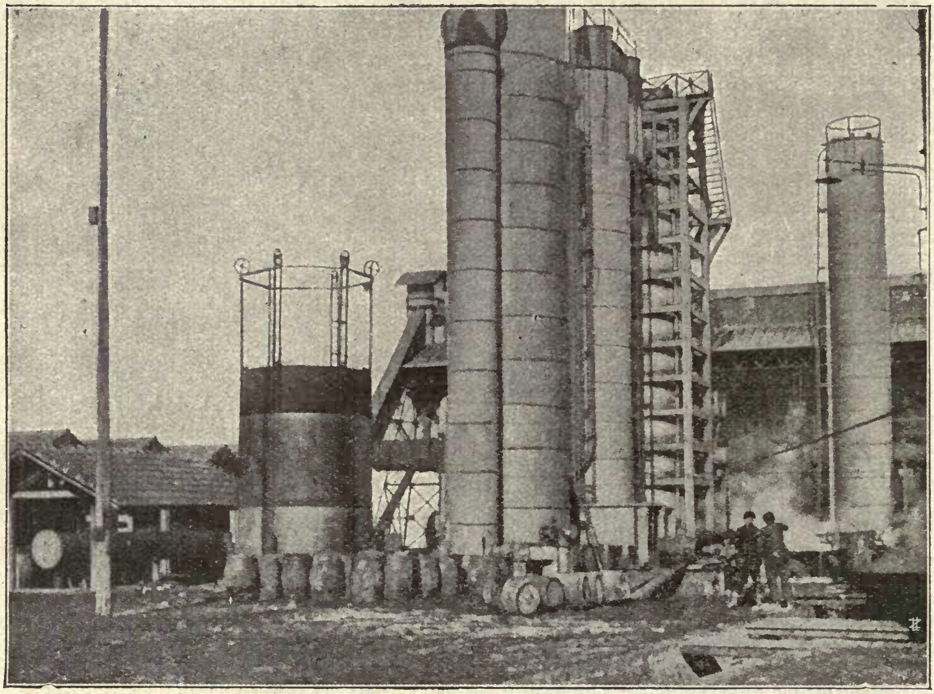


Fig. 142.—Absorption and washing tower and gasometer for peat gas at Codigoro.

The sulphuric acid collecting at the bottom of the leaden tower is pumped repeatedly to the top until rich in ammonium sulphate and is then passed into a vessel which feeds the concentration apparatus, fresh sulphuric acid being introduced into the tower. The water collecting at the bottom of the third tower, after being freed from tar, is pumped on to a fourth tower (of iron; to the right of Fig. 142) to moisten and heat a current of air which is introduced at the bottom and is then superheated together with steam and passes along a wide tube furnished with an air-meter to the producers where the Mond gas is produced. A consumption of 6000 kilos of steam per hour is required to gasify 6000 kilos of peat per hour. The only turbo-alternator for the production of power for the whole works (about 1000 amps. at 225 volts) absorbs from 16 to 20 kilos of steam per kilowatt-hour, and the total daily output is 7000 kilowatt-hours, all derived from the combustion of part of the Mond gas produced.

From Codigoro peat a yield of 80 kilos of ammonium sulphate per ton of dry peat, with a consumption of about 100 kilos of sulphuric acid of 56° Bé., was anticipated.

The Codigoro plant started working in June 1913, but owing to various contretemps and unforeseen difficulties, to bank charges and inherited indebtedness, work was partially suspended in 1915. At the end of 1916 the company was reorganised and separated from the Orentano establishment, which was developed, enlarged, and improved (1917) by the Società Italiana Prodotti Esplodenti. At Codigoro work was again started at the end of 1915, but proceeded irregularly, in spite of the high price of ammonium sulphate during the European War, and in rotating reels throw up a fine spray of water, which washes the gas and cools it to about 90°. Thence the gas passes along a wide horizontal tube to the lower part of the leaden tower *D*, filled with bricks or earthenware rings down which falls a spray of ammonium sulphate solution containing a certain amount of sulphuric acid. The solution which has fixed the ammonia of the gas collects in the labyrinth tank, *E*, part being then withdrawn and the rest diluted with fresh sulphuric acid (in *H*) so as to bring the density to its original value, and then forced by the pump, *I*, through the tube *K* on to the tower *D*. The ammonium sulphate solution withdrawn from *W* is concentrated and neutralised with ammonia, ammonium sulphate crystals (dark grey owing to the presence of small quantities of tar carried by the gas) being thus separated.

The gases from the top of the tower *D* are led to the base of the water tower *F*, filled with brick sprayed from the top with water, which cools the gas and condenses the excess of water vapour still present. After filtration through wood chips or shavings (changed once a month) to remove a little water the gas is carried to the gasometer or direct to the hearth or burners. The tepid water which collects at the bottom of the tower *F* is pumped (*n*) to the top of the third air tower, *G*, in which it falls as a spray, meeting and saturating with moisture a current of air from a fan, *q*, the air then serving to feed the gas-producer, *A*, as mentioned above. The cold water collected at the bottom of the tower *G* is pumped (*O*) to the cooling tower, *F*.[1]

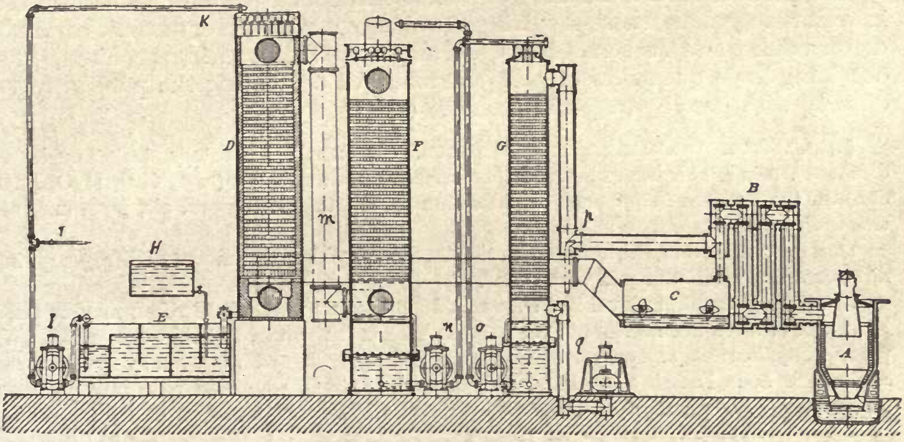


FIG. 143.

1916 and 1917, owing to the great scarcity of all fuel in Italy, the Codigoro Company preferred to sell bricks of compressed peat at £6 16*s*. per ton.

In 1910 a peat-gas plant was erected at Osnabruck (Hanover) to produce 4000 electrical h.p. (800 h.p.-hours per ton of peat and about 60 kilos of ammonium sulphate per ton of dry peat).

In 1911 a plant with Körting gas-producers started work at Ottawa.

[1] To start up the plant, shavings are burnt for two or three days in the producer, a little coke being mixed in and a little air blown in, the gases being allowed to escape until they contain 30 per cent. of combustible gas. When the producer is working regularly, its action may be slowed down by diminishing the air blast, charging the producer completely, and allowing it to work more and more slowly until the first part of the tube of the gas cooler is choked with water and the gas escapes into the air; in this way it may be kept alight for a fortnight and started vigorously again when required.

Mond producers have been improved by Messrs. Crossley Bros., Ltd., (of Manchester) and in England they are used especially to utilise bituminous coal waste, Mond gas being obtained intermediate in composition to air gas and water gas and similar to Dowson gas; nowadays such intermediate gases are termed poor gas or motor gas (*see* chapter on Carbon Monoxide). One of the first plants (at Winnington, Cheshire) for utilising bituminous coal waste (68 per cent. C, 1·3 per cent S, 1·3 per cent. N, 14·7 per cent. H and O, 7·2 per cent. H_2O, 7·5 per cent. ash) gave the following results: to burn 1 ton of this coal, 3000 kilos of air (about 3800 cu. metres) were injected into the air tower, *G*; this absorbs 1000 kilos of water at 70°, and before its heat is recovered in *B* (Fig. 143) it is treated with a further 1500 kilos of steam, so that for 1 ton of coal a total of 5500 kilos of air and steam at 85° are injected. The gas leaves *B* at 250° and enters the producer, which it leaves with a temperature of 450° as a mixture of 4500 kilos of gas and

Ekenberg suggests the carbonisation of peat in autoclaves under pressure.

Effront beats up the peat with 6 to 7 per cent. of water and 2 to 3 kilos of sulphuric acid per 100 kilos of peat, and heats the mass under pressure at three atmospheres; he then renders it alkaline with lime, and at 43° adds 50 grms. of aluminium sulphate, 20 grms. of superphosphate and considerable quantities of yeast cultivated in extracts of molasses or of cereals (Ger. Pat. 215,531 of 1908). When the fermentation is completed the alcohol is distilled and collected separately from the ammonium salts. In a similar manner Effront obtains ammonia and organic acids from the residues of distilleries which contains amino-acids. In 1911 a large company was founded to exploit Effront's process, but serious technical difficulty was encountered.

IV. SYNTHETIC AMMONIA FROM ATMOSPHERIC NITROGEN. The problem of synthetic ammonia is bound up with the enormous problem of the fixation of atmospheric nitrogen, and is of great importance to agriculture (*see* pp. 347 *et seq.*).

The production of ammonia from atmospheric nitrogen has now been solved in various ingenious ways—by fixing the nitrogen on metals or metallic carbides, or on oxides and carbonates and decomposing the resulting products, thus obtaining large quantities of pure ammonia, or by uniting the pure nitrogen directly with pure hydrogen in presence of a catalyst.

(*a*) CALCIUM CYANAMIDE AND NITRIDES. In small laboratory tests made at different times it had been observed that certain metallic oxides (*e. g.*, CaO, MgO, BaO, etc.), in the hot and in presence of potassium carbonate solution and air, form minimal traces of potassium nitrite and nitrate.

Metallic magnesium, lithium, etc., in the hot fix a considerable amount of nitrogen giving nitrides which yield ammonia with water.

Margueritte and Sourdeval had shown in 1862 that atmospheric nitrogen may be fixed by means of a red-hot mixture of carbon and barium carbonate, but the process found no practical application, and only in 1906 was it taken up again and improved by the Badische Anilin und Soda-Fabrik (Ger. Pats. 190,955 and 197,394), who used pure nitrogen at a temperature of about 1500°, obtaining 60 per cent. of barium cyanide, $Ba(CN)_2$, and 40 per

---

2000 kilos of steam; from the counter-current heater it issues at 280° and from the washer (*C*, Fig. 143) at 90° after having absorbed a further quantity of 750 kilos of water, so that 4500 kilos of gas and 2750 kilos of steam [about 38 per cent. of steam, whereas saturation would require 64 per cent.; at 90° the vapour pressure of water is 525 mm., so that the partial pressure of the dry gas is 235 mm. (760–525). Since 1 cu. metre of Mond gas at 0° and 760 mm. weighs 1 kilo, at 90° and 235 mm. it will weigh 0·241 kilo, while the water vapour will weigh 0·424 kilo; hence for saturation $424 \div (424 + 241) = 64$ per cent. of steam is required] enter the acid absorption tower *D*. This gas should not be saturated with moisture, since water would then be separated in the tower *D*, and would dilute the ammonium sulphate solution, which is to be avoided. From the sulphuric acid tower the gases issue at 80° and from the cooling tower, *F*, (Fig. 143) at 65°, after having deposited about 1500 kilos of water vapour; thus, 5750 kilos of moist gas remain with 22 per cent. of moisture (*i. e.*, 1265 kilos of water), which is the saturation proportion at this temperature. The water feeding the cooling tower enters at the top at 50° and collects at the bottom at 80°; it is then used for feeding the air tower, *G* (to heat and moisten the air for the gas producer) and here collects below at 50°, so that it can be again used for the cooling tower, *F*, and so on. In the acid tower, *D*, the solution does not heat, but remains at about 80°.

The Mond gas of this Winnington plant has the following mean composition in the dry state: 10·2 per cent. CO, 16·3 CO_2, 26·4 H, 2·5 CH_4, and 44·6 N, its weight being 1·015 kilo per cu. metre and its calorific value 1300 cals. Since 1 ton of waste coal (of calorific power 7200 cals.) gives 4485 kilos of dry gas (*i. e.*, 5750 —1265) or about 4500 cu. metres (4·5 cu. metres per kilo of coal), the gross calorific yield of Mond gas per kilo of coal used is $(4{\cdot}5 \times 1300) \div 7200$, *i. e.*, 81·2 per cent. The production of 4·5 cu. metres of Mond gas requires, however, 1·5 kilos of steam (*see above*), and this consumes about 0·214 kilo of the waste coal (assuming that 1 kilo of coal gives 7 kilos of steam in the boiler); account must be taken of the amount of the Mond gas consumed in the engines for driving pumps (about 2·5 cu. metres per h.p.-hour, corresponding with 0·6 kilo of the waste coal) and as these require altogether 30 h.p., 18 kilos of coal per hour are consumed during the gasification of 1 ton of coal, or 0·018 kilo per kilo of coal gasified. Hence, to produce 4·5 cu. metres of Mond gas, $1 + 0{\cdot}214 + 0{\cdot}018 = 1{\cdot}232$ kilos of coal are required, so that the nett calorific efficiency will be $(4{\cdot}5 \times 1320) \div (1{\cdot}232 \times 7200) = 0{\cdot}66$. Thus, the final yield is 66 per cent. of the theoretical value of the coal used, and as this is usually of poor quality such a yield may be regarded as satisfactory.

cent. of barium cyanamide, BaN·CN, this mixture being converted completely into barium cyanide by treatment with acetylene in an iron retort at 600–800°.

In 1911 L. Petit Devaucelle (Ger. Pat. 247,451 and French Pat. 429,140) introduced improvements into the Margueritte process, hard lumps of very pure agglomerated carbon (*e. g.*, petroleum coke free from silica and alumina) being heated with baryta in retorts at 900°, currents of nitrogen and steam alternating every 5–6 minutes; this procedure leads to the formation on the surface of the carbon of a skin of barium cyanide, which yields ammonia directly with steam. Attempts made in France to utilise this process gave no practical result; in 1916–1917 tests were also made in Italy.

The barium carbonate may be replaced by titanic acid, the product obtained yielding cyanide and cyanamide if fused with a flux in presence of alkali or alkaline earth. In 1879 Basset obtained boron nitride by the action of nitrogen on boric acid in presence of carbon.

O. Frank (Ger. Pat. 248,697, 1911) suggested the use as a nitrogenous fertiliser of a mixture of calcium and silicon nitrides, obtained by passing a current of nitrogen (oxygen-free) over a mixture of quicklime (6 kilos) and silicon (10 kilos) heated to 700°, the temperature rising to 1050° during the reaction.

During recent years the industrial world has taken great interest in the Serpeck process for fixing atmospheric nitrogen as aluminium nitride, which with water yields ammonia and aluminium hydroxide quantitatively. In 1896 Wilson and then Mehmer obtained nitrides of Al, Ca, Ti, Si, Mg, and V, starting from the elements, but the yields were unsatisfactory, whereas Serpeck obtained almost quantitative yields by reducing alumina with carbon in presence of nitrogen[1]: $Al_2O_3 + 3C + N_2 = 2AlN + 3CO - 217{,}500$ cals.; the thermal effect is the resultant of 385,800 cals. necessary to dissociate Al_2O_3, 90,000 cals. given by the exothermic formation of 2AlN and 78,300 cals. given by the formation of 3CO. The velocity of this reaction is scarcely appreciable at 1000°, increases rapidly up to 1500°, and is great at 1800°, the reaction being very vigorous at 1850° and ceasing at 2100°, as the decomposition pressure of the nitrogen in the aluminium nitride is then greater than the partial pressure of the nitrogen in the gaseous mixture entering the reaction furnace. Serpeck started his experiments in 1905 (Ger. Pats. 181,992, 183,702, 206,588, 216,746, 224,628, 231,886 and 235,213, 204,875, 238,340, 241,339, 244,651, 246,419, 248,054, etc.) and made the important discovery that oxide of iron, which usually contaminates natural alumina (bauxite), effects a catalytic acceleration of the reaction even at 1600-1700° (or lower), almost all the aluminium being found as nitride with 30 per cent. of combined nitrogen.

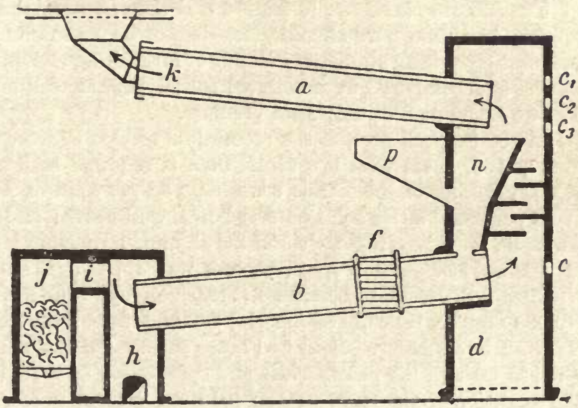


FIG. 144.

In practice the reaction is carried out in revolving furnaces almost identical with those used in artificial cement factories (*see* illustrations in chapter on Portland Cement) and shown diagrammatically in Fig. 144. The intimate mixture of crude bauxite and finely powdered carbon passes down the first branch of the inclined tubular furnace, *a*, where it undergoes a pre-heating by the combustion of the gases from the second branch, *b*, in which the mass from *a* meets the gases (at 400–500°) of the gas producer, *j*—containing 70 per cent. of N and 30 per cent. of CO—and the reaction takes place at about 1600°. The nitride formed falls into the cooling chamber, *h*, where it sets to a crystalline

---

[1] At first Serpeck tried to reach aluminium nitride in stages, passing through aluminium carbide: $Al_4C_3 + Al_2O_3 = 3CO + 6Al$, which in presence of nitrogen would yield AlN. He had, however, to use excessively high temperatures to form the aluminium carbide (from Al_2O_3 and carbon), and the final yields were always low.

mass, while the gases which have given up the nitrogen are enriched in CO (up to 70 per cent.) and pass up the tower *d*, the calculated amount of air entering through the adjustable orifices, $C_1 - C_4$; the gases then burn in the tube *a*, raising the temperature to about 1300°. In order that the formation of nitride may be complete the temperature is raised at the point *f* of the second tube by means of an electrical resistance. To obtain good yields, the gas from the producer should contain as little CO_2 as possible.

The revolving furnace, *a*, which makes less than one turn per minute, consists of a wrought-iron cylinder coated inside with refractory material, while in the second tube, *b*, where higher temperatures are reached, the refractory lining is covered with a layer of aluminium nitride which resists the great heat still better and is a poor electrical conductor. Theoretically, 82 kilos of aluminium nitride can be prepared with 248 kilowatt-hours, *i. e.*, 3 tons per kilowatt-year, which is equivalent to 1 kilowatt-year per 1000 kilos of nitrogen combined or 1 kilowatt-hour per 115 grms. of nitrogen combined. Practically, at most 70 grms. of nitrogen are fixed per kilowatt-hour, whilst with the electric furnace 13 grms. of nitrogen are fixed as oxide of nitrogen (*see later :* chapter on Synthetic Nitric Acid) and as calcium cyanamide 45 grms. are fixed per kilowatt-hour.

To obtain ammonia from the aluminium nitride (which is obtained almost in powder and needs no special crushing), the latter is charged into large autoclaves provided with stirrers in which dilute caustic soda solution is heated under pressure, the ammonia gradually distilling off through suitable valves: $AlN + 3NaOH = NH_3 + Al(ONa)_3$.

The sodium aluminate is filtered and then decomposed by hydrolysis as in the Bayer process to obtain pure alumina (*see* chapter on Aluminium), which may be used for the preparation of fresh aluminium nitride or for making aluminium; in this case the aluminium nitride is decomposed in autoclaves containing the sodium aluminate solution at 20° Bé. for two hours at 2 atmospheres pressure.

In the Serpeck process the aluminium nitride is decomposed (according to Norwegian Pat. 23,290, 1912) with less alkali than is required to form potassium aluminate (Al_2O_3, K_2O), 100 kilos of the nitride containing 82 per cent. of AlN being treated with 200 kilos of 20 per cent. KOH solution and boiled and stirred under pressure; by this means the ammonia is evolved regularly and the alumina remaining serves to dissolve a fresh quantity of the nitride. The Serpeck process was applied in 1912 by the Société Génèrale des Nitrures a S. Jean de Maurienne (French Savoy) with furnaces consuming 2500 kilowatts (10,000 ampères) each. In America 8000 kilowatt furnaces were made, 70 metres long and 3 metres in diameter. Both in France and in America enormous difficulties were encountered in making the plants work, and speculation in the shares of the company aggravated the condition of affairs, so that in 1915 the Serpeck process resolved itself into a failure.[1] It is capable of future application only when the aluminium hydroxide is of value for making aluminium or its sulphate; in such case the nitrogen of the ammonia would cost about 3 — 3·5*d.* per kilo, whereas that of sodium nitrate or ammonium sulphate costs up to 1*s.* 2·5*d.* or more per kilo and that of calcium cyanamide about 10*d.* per kilo.

In 1895 Frank and Caro (Ger. Pat. 88,363) took out patents for the preparation of cyanides by the absorption of atmospheric nitrogen, mixed with steam, by barium carbide heated to 700–800°. The process was then simplified by two other patents (Ger. Pats. 92,587 and 95,660), but in 1898 (Ger. Pats. 108,971, 116,087, and 116,088, and Eng. Pat. 25,475) it was found that during the reaction only traces of cyanide are formed and that the product is almost exclusively barium cyanamide: $BaC_2 + N_2 = NC \cdot NBa + C$.

If the barium carbide is used in large lumps, barium cyanide is formed in preponderance, but if small granules are employed, about 30 per cent. of cyanide is obtained, the rest of the product being barium cyanamide; when, however, the latter is fused with alkali salts (*e. g.*, NaCl) and carbon, it is converted quantitatively into barium cyanide: $BaN_2C + C = Ba\ (CN)_2$. This process was employed industrially—for the manufacture of sodium and potassium cyanides for gold extraction—by the Gold-und Silbernheiden-Anstalt of Frankfort (Ger. Pat. 212,706).

The process became more economical when Pfleger, Rothe (1898), and Freundenberg showed that calcium carbide may be employed instead of barium carbide and absorbs 85 to 95 per cent. of the theoretical amount of nitrogen at 1000° to 1100° and forms not cyanide, but only calcium cyanamide; the yield increases with the pressure of the nitrogen.

---

[1] It appears that the Serpeck patents were sold in America for £320,000, and the £20 shares were sold at as much as £216, but fell below par in 1915.

It was then found that it is not necessary first to prepare calcium carbide, but that a single operation suffices in which the ingredients which serve for the preparation of the carbide itself are heated in the electric furnace in presence of nitrogen: $CaO + C_2 + N_2 = CO + NC{\cdot}NCa$ (calcium cyanamide). The atmospheric nitrogen is first freed from oxygen by passing air over red-hot copper. By means of this direct reaction a blackish product of crude cyanamide is obtained containing only 12 to 14 per cent. of nitrogen, since at 1380° the reaction begins to be reversible. When the carbide is used the crude product contains 20 to 22 per cent. of nitrogen. This substance, which is very well adapted for the preparation of pure potassium or sodium cyanide by fusing it with the corresponding alkali chloride, was first manufactured by the Cyanid Gesellschaft of Berlin under the direction of Caro, Frank, and Erlwein, at the Siemens and Halske works at Martinikenfeld, near Berlin. The nitrogen should be free from oxygen and especially from CO, since otherwise carbide is lost: $CaC_2 + CO = CaO + 3C$. Nitrogen is nowadays obtained more economically from liquid air (*see* p. 342). The excellent results which have been obtained with these substances as nitrogenous fertilisers are of great interest (Ger. Pat. 154,505, February 1902). The agricultural experiments independently conducted by Wagner and Gerlach have shown that the nitrogen in crude calcium cyanamide has the same fertilising value as that in ammonium sulphate and is equal to 90 per cent. of that contained in sodium nitrate. Naturally the effects of this new fertiliser vary with the nature of the soil; thus in peaty, sandy, or marshy soils or soils rich in humus satisfactory results have not so far been obtained. On the other hand, it gives good results on calcareous or clay soils. Since it is harmful to the germination of seeds and to young vegetation, especially during the dry and hot weather, it is advisable to spread it over the soil 10 to 15 days before sowing, and then to start ploughing and harrowing immediately. It is rather harmful to meadows because it cannot be mixed with the soil. An excessive amount of moisture is also prejudicial to the action of this manure, although in Italy good results have been obtained with it in rice fields.

Calcium cyanamide is decomposed (according to Löhnis, 1905) by various bacteria in the soil into ammonia and calcium carbonate. Recent experiments of Immendorf (1905), Pozzoli, Ulpiani, and Fascetti (1906) show that calcium cyanamide reacts with carbon dioxide in the cold to form ultimately calcium carbonate and *dicyandiamide* ($C_2N_4H_4$), which is not injurious to seeds or vegetation and undergoes ammoniacal fermentation. If, on the other hand, it is acted on by carbon dioxide and water at temperatures higher than the ordinary temperature, the final products are calcium carbonate and cyanamide ($NC{\cdot}NH_2$), which is poisonous and unfermentable, but capable of forming ammonia in the more harmful nascent state. Soils containing much lime facilitate the former reaction. In opposition to the general opinion Perotti in 1907 maintained that cyanamide is not injurious to vegetation.

In 1910 C. Ulpiani showed that in the soil calcium cyanamide is first transformed into urea by the action of certain colloidal substances which act as catalysts (aluminium or ferric hydroxide gel, or the gels of hydrated silicates, such as zeolites), and that if the soil were calcined it would no longer transform the calcium cyanamide, owing to lack of colloids. In a second stage, perhaps through the action of microbes, it is transformed into ammonium carbonate. Dicyandiamide may be formed before urea, but is immediately decomposed by the earth, forming urea. Calcium cyanamide does not give satisfactory results in sandy soils, since colloids are lacking, or in peaty soils, where suitable bacteria (Eumycetes) are not present.

Calcium cyanamide may be mixed with potassium salts, or with basic slag, but not with superphosphate, because it then causes a portion of the phosphoric acid to become insoluble; it does no harm when employed for the manuring of rice fields. When mixed with sodium bisulphate calcium cyanamide gives a good nitrogenous manure. Calcium cyanamide has the disadvantage that it develops acetylene when moistened, but this fault may be remedied by granulating the fresh product with a little water (3 to 4 per cent.), which immediately decomposes the small amount of calcium carbide still present; by this means it hardens and may be broken without giving powder in the air (Ger. Pat. 231,646, 1910). When moisture and CO_2 are absorbed, the weight increases and the proportion of nitrogen is thus lowered, but ammonia is not lost. Calcium cyanamide must not now contain more than 0·2 per cent. of carbide, and explosions due to formation of acetylene do not occur nowadays. L. Londei (1912) renders calcium cyanamide insensitive to moisture by powdering it in presence of graphite. Birkeland in 1908 proposed the absorption of nitrogen dioxide (NO_2) prepared in the electric furnaces by calcium carbide, which is thus transformed into calcium nitrate and ammonium nitrate, containing about 25 per cent. of nitrogen.

The calcium cyanamide industry did not prove to be sufficiently economical in Germany, because the electrical power required for the production of the calcium carbide and for the separation of the atmospheric nitrogen was too costly.

Italy was the country which produced calcium carbide at the lowest price, and in Italy, therefore, through the initiative of the Electro-Chemical Company of Rome, the Società Italiana per la Fabbricazione dei Prodotti Azotati was formed in 1904 with a capital of £280,000 to prepare calcium cyanamide on a vast scale by utilising electrical energy at Piano d'Orte, where it costs only £2 per h.p.-year. This large establishment commenced work in October 1905, and in 1907 the production was 1200 tons, and in 1909, with new retorts, 2200 tons; in 1912, in the new works at Collestatte (*see later*) the output reached 8600 tons, and in 1913 it exceeded 11,400 tons.

In these works retorts were first used which were similar to those employed in the manufacture of lighting gas (*see* Vol. II., "Organic Chemistry"), but constructed of steel. The nitrogen was produced, more cheaply and purer, from liquid air. The retorts proved to be unserviceable after a short time and were renewed, but the results obtained were not much better. The form of the retorts was completely changed in 1908 and 150 vertical retorts were constructed, 1·4 metres high and 1 metre wide, each holding 400 kilos of calcium carbide, whilst the old horizontal retorts only contained 100 kilos; the mass was heated by producer-gas with frequent stirring. These new retorts were heated by electric resistance, starting from the centre by means of an arm of graphite (Fig. 145); thus the heat was propagated gradually from the centre towards the circumference, that produced by the exothermic reaction being also used. The heating was interrupted at a certain stage in order to prevent the temperature from becoming excessive and so reversing the reaction; the heating was continued for twenty-four hours at 800° to 1000°, the nitrogen current being maintained for thirty-five hours. In twenty-four hours a compact homogeneous mass containing 20 to 21 per cent. of nitrogen is obtained; this is then powdered and granulated by means of a spray of a weak aqueous solution of glue or of tar-oil. In this way the small amount of unchanged carbide is decomposed and the mass does not become powdery when spread over the soil, and does not develop acetylene. Tofani (Ger. Pat. 246,077, 1910) proposed the use of a vertical cylindrical furnace to work continuously, powdered carbide being dropped from the top and the nitrogen rising from below.

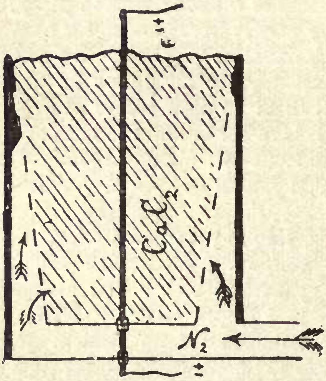


FIG. 145.

In 1911 the manufacture of calcium cyanamide at Piano d'Orte was suspended, and the large works at Collestatte were started; these, with other factories, produced 15,556 tons in 1914 and 25,292 tons (worth £284,645) in 1915, a good deal of the product being used for the manufacture of ammonia, nitrate, and ammonium sulphate. During the European War, cyanamide was used in various countries for making ammonia to be oxidised by the Ostwald process (*see later*) to nitric acid for explosive works. Before the war Germany produced 18,000 tons of calcium cyanamide per annum, whereas in 1916 the output reached 450,000 tons. In France, at the beginning of 1917, 30 tons per day of synthetic nitric acid were produced at Angoulême alone by oxidising ammonia prepared from calcium cyanamide.

The cost price of calcium cyanamide is about 9·5*d.* per unit of nitrogen and it is sold at 11·5–13·5*d.*, whilst the unit of nitrogen in ammonium sulphate is sold at 14·4*d.* and that in sodium nitrate at 15·4*d.*[1] In spite of all these improvements this industry does not

---

[1] The cost of 1 ton of calcium cyanamide containing 20 per cent. of nitrogen and formed from 800 kilos of carbide in this Italian works, of which the patent alone is valued at £80,000, may be calculated approximately for an annual production of 10,000 tons from the following

prosper, because agriculturists still have doubts, and further endeavours are now being made to decompose calcium cyanamide with steam, so liberating the ammonia and manufacturing ammonium sulphate.

In Europe in 1908 there were eleven large works of the total capacity of 170,000 tons, but the actual production was less than 40,000 tons.[1]

Although the cyanamide process is still in its infancy mention must be made of certain improvements, especially those of F. Polzenius, which form the subject of a patent (Ger. Pat. 163,320, Nov. 1, 1901), in which it is shown that on adding about 10 per cent. of calcium chloride to the powdered calcium carbide the fixation of nitrogen occurs at temperatures of 700° and with increased rapidity. The chloride acts as a flux and accelerator of the reaction. This product has been manufactured since 1905 by the Nitrogenous Fertiliser Company of Westeregel in Germany—Stickstoffdünger Gesellschaft—which has a production of 5000 tons annually and is already erecting further works for a larger production. The new product is almost identical with calcium cyanamide; it is commercially called Stickstoffkalk or nitro-lime.[2] It is stated (Ger. Pats. 203,308 and 227,854) that the yield of calcium cyanamide is increased if 9–10 per cent. of the cyanamide is mixed with the carbide used.

Carlson has used 10 per cent. of calcium fluoride as a catalyst since 1906; the resulting calcium cyanamide is not as hygroscopic as that prepared with calcium chloride.

In 1907 E. and G. Pollacci proposed the preparation of calcium cyanamide with greater ease and of greater manurial value by employing 4 per cent. of potassium carbonate as a catalyst. They also proposed to treat this calcium cyanamide with sulphuric acid in order to obtain a fertiliser with an ammonium sulphate basis, this no longer having the caustic action of ordinary calcium cyanamide (Ger. Pat. 210,808). Förster, Jacobi, and Bredig (1907) showed that chemically pure calcium carbide does not combine with nitrogen, but that the presence of lime induces the reaction.

VARIOUS USES OF CALCIUM CYANAMIDE. Owing to the prejudice of many farmers and to slight defects still occurring in calcium cyanamide, a good deal of this is now used for making ammonium sulphate for fertilising purposes, but with time this irrational, vicious circle will be abandoned. The transformation of calcium cyanamide into ammonia (for the manufacture of synthetic nitric acid, nitrate and ammonium sulphate) was suggested by Frank (Ger. Pat. 134,289), who treated the crude material with superheated steam: $CaN_2C + 3H_2O = CaCO_3 + 2NH_3$; with hot water alone, dicyanodiamide is formed: $2CaN_2C + 4H_2O = (CN\cdot NH_2)_2 + 2Ca(OH)_2$. According to Ger. Pat. 236,705, 99 per cent. of the nitrogen is transformed into ammonia by hot water at 3 atmos., if a counter-current apparatus similar to the Savalle alcohol column is used. It seems, however, more convenient to use water under pressure at 180° (Austrian Pat.

---

figures: 800 kilos of calcium carbide are required at £4 16*s.* per ton = £3 16*s.* 8*d.*; 200 kilos of nitrogen at 1·92*d.* = £1 12*s.*; redemption of capital invested in plant, patents, etc., £1 4*s.*; interest at 5 per cent. on the capital, £1 4*s.*; cost of labour, technical supervision and administration, about 6*s.* 5*d.*; cost of power, including water, coal, light, lubricants, etc., 4*s.* 9½*d.*; general expenses, repairs, packages, unforeseen circumstances, losses, etc., 4*s.* 9½*d.*; total cost per ton, £8 12*s.* No account is taken of the possible utilisation of oxygen or of the practical yield compared with the theoretical, as we have taken the theoretical yields.

The sale price of calcium cyanamide in France in 1910 was £9 per ton for that containing 15 per cent. N, and 14·2*d.* per unit for that with 17 to 20 per cent. N. In Germany in 1914 that with 17 to 22 per cent. N was sold at 13·9*d.* per unit.

[1] The total capacity (not actual production) of all the calcium cyanamide factories in the world in 1913 was 281,000 tons per annum.

[2] A sample of commercial calcium cyanamide—Kalkstickstoff (I)—and another sample—Stickstoffkalk (which is blacker, has a tarry odour, and is not readily wetted by water)—gave the following results on analysis:

	I	II		I	II
Total nitrogen . .	19·21%	18·00%	Iron and alumina . .	2·10%	2·70%
Ammoniacal nitrogen .	0·12%	0·12%	Carbon	13·94%	14·6%
Chlorine (as cal. chloride)	—	3·75%	Sand and soluble silica	2·94%	2·64%
Total lime (CaO) . .	54·85%	56·20%	Ether extract . .	—	6·62%
Magnesia (MgO) . .	0·07%	0·45%	Water	0·26%	0·60%

In order to obtain concordant results in the determination of nitrogen by the Kjeldahl method, the following procedure is employed: 1 grm. of the substance is treated with 30 c.c. of a cold mixture of equal volumes of sulphuric acid and water together with a drop of mercury; the heating is carried out in the ordinary flasks for 1½–2 hours and the liquid diluted and distilled as usual, the ammonia being absorbed in 20 c.c. of normal sulphuric acid.

42,810) and to pass the vapours evolved into a dephlegmator from which the ammonia is drawn off continuously while the condensed hot water is again circulated. According to Austrian Pat. 36,444 and Ger. Pat. 198,706, the evolution of ammonia is facilitated by addition of calcium chloride solution. When calcium cyanamide is fused with sodium chloride and the mass lixiviated, gaseous hydrogen cyanide is liberated and may be absorbed by caustic soda solution to form sodium cyanide, which is in demand for the extraction of gold. It is used for hardening iron as a partial substitute for yellow prussiate, which carburises the iron at the surface; for this purpose it is mixed with other substances and sold under the name of *ferrodur* (*see* Cementation of Iron and Mild Steel). Calcium cyanamide serves for the preparation of cyanamide (required for the synthesis of many organic compounds), dicyanodiamide, dicyanodiamidine salt (used as a retarder in the manufacture of safety explosives), guanidine compounds and urea (used for preparing various organic compounds, *e. g.*, thiourea, which is used for the preservation of dyed silk (*see* Vol. II., "Organic Chemistry"). Dicyanodiamidine sulphate serves for the separation of nickel from cobalt in alkaline solution, nickel giving a yellow crystalline precipitate. Calcium cyanamide is used also for the preparation of veronal (*see* Vol. II., "Organic Chemistry").

(*b*) AMMONIA FROM NITROGEN AND HYDROGEN. This synthesis has been applied industrially only since 1912, as a result of rigorous and careful investigations commenced by Haber in 1904, continued with Le Rossignol in 1908, and completed and applied practically with the technical and financial co-operation of the Badische Anilin und Soda-Fabrik.[1]

The equation of the equilibrium between N, H and NH_3 in the reversible reaction, $N_2 + 3H_2 \rightleftarrows 2NH_3$ (*see* pp. 65, 69 and 320) will be:

$$K = \frac{(NH_3)^2}{(N_2)\,(H_2)^3}.$$

Recalling the equation for the gaseous state (p. 26) and the proportionality between pressure and molecular concentration (p. 65), we have $K\frac{1}{R^2T^2} = \frac{q^2}{p_1p_2{}^3} = K$, where q, p_1, and p_2 are the partial pressures of the ammonia, nitrogen, and hydrogen respectively. This new constant of proportionality, K, depends on the temperature, and if C_{NH_3}, C_{N_2}, and C_{H_2} indicate the relative molecular concentrations (*see* p. 65) of the three gases and P the total pressure of the mixture (*i. e.*, $q + p_1 + p_3$), we have:

$$P\sqrt{K} = \frac{C_{NH_3}}{C_{N_2}^{\frac{1}{2}} \cdot C_{H_2}^{\frac{3}{2}}},$$

that is, the concentration of the ammonia in the conditions of equilibrium and for each temperature increases with the pressure. The influence of temperature on the equilibrium concentrations (*see* pp. 67, 68 and 379) being given by the differential equation, $\frac{d \log K}{dt} = \frac{Q}{RT^2}$ (Q is the molecular heat of formation of ammonia from its elements and R the ordinary gas constant), the most convenient temperature for the formation of ammonia may be determined.

The reaction being exothermic and Q positive, we have:

$$N_2 + 3H_2 = 2NH_3 + 2 \times 11{,}890 \text{ cals.}$$

Hence the maximum concentration of NH_3 will be obtained at the lowest temperature compatible with a reaction velocity that gives an industrial yield (*see later:* Synthetic

---

[1] The formation of traces of ammonia from the elements by the action of the electric discharge had already been observed by numerous investigators [Regnault, Deville, Berthelot, Young and Ramsay (1884), etc.], but the sluggish action of the nitrogen and the ready dissociation of the ammonia, even at temperatures not very high (incipient red), gave little hope for the manufacture of synthetic ammonia. Perman, however, showed in 1904 that certain catalysts have a great influence on the formation of NH_3 from the elements, and on its dissociation. Haber and van Oordt (1904) found that at 1000°, 99·8 per cent. of the ammonia is dissociated, and that only at about 300° is the dissociation maintained within practically useful limits (90 per cent.). In 1907 Nernst and Jost obtained a concentration of 0·9 per cent. of ammonia (from its elements) by working at 700° and 50 atmospheres in presence of manganese, but they did not regard the process as of practical value.

Nitric Acid) and with the highest pressure possible. At 100 atmos. the concentration of NH_3 is about 100 times as great as at 1 atmos.; thus:

At 800° with a pressure of 1 atmos. (NH_3) is 0·011%, at 100 atmos. 1·1%
„ 600° „ „ „ „ „ 0·048%, „ „ 4·5%
„ 500° „ „ „ „ „ 0·13%, „ „ 10·8%

In any case, however, the reaction is extremely slow, and it was on this account that Haber studied the action of various catalysts which, without displacing the equilibrium, considerably accelerate the reaction and lower its temperature. Thus, pulverulent iron causes a convenient acceleration at 700°, whilst osmium and uranium do so at 500° (the dissociation of the NH_3 being less: Ger. Pat. 223,408). Of the numerous catalysts and activators yet proposed,[1] the only one apparently applied in practice is iron, great care being taken in the purification of the gas so as to eliminate catalyst poisons (*see* footnote), which may be derived even from the tubes themselves or from traces of lubricating oil from the gas compressors; electrolytic hydrogen sometimes contains traces of mercury vapour. To eliminate these poisons the gases are filtered, washed, dried, and then passed over alkali or alkaline-earth metals. If the catalyst does become poisoned, its original activity may sometimes be restored by oxidising it in the hot or by adding bases or basic salts and then reducing the whole with hydrogen in the hot.

Industrial plants for the preparation of synthetic ammonia are kept secret and their construction presents very great difficulties. Thus, it was found that the iron used, which should withstand great pressures (up to 150–200 atmos.) at high temperatures (500–700°), not only underwent change and became less resistant, but also allowed the rapid diffusion of hydrogen through its pores. The Badische Company (Ger. Pats. 254,571 and 256,296) succeeded in overcoming these difficulties and in counterbalancing the effects of the pressure

---

[1] Haber took out another patent in 1909 (Ger. Pat. 238,450): ammonia of 2 per cent. concentration was obtained at 700° and at 175 atmos., powdered iron being used as catalyst; succeeding patents were taken out in conjunction with the Badische Anilin und Soda-Fabrik. According to Ger. Pat. 235,421, N_2 and $3H_2$ are made to react at a constant pressure, the ammonia being eliminated with considerable cooling and the heat of the reaction being used to heat the initial gases. Ger. Pat. 252,275 claims that the use of the most suitable catalysts gives higher concentrations of ammonia and that it is not necessary to recover the heat of the reaction or to maintain the pressure constantly (with osmium as catalyst, Haber obtained a concentration of 8 per cent. of NH_3 by volume at 175 atmos.); however, all the osmium found in the world would suffice for only a small part of the ammonia necessary to agriculture. According to Ger. Pat. 229,126 the osmium may be replaced by uranium, which at 580° and 190 atmos. gives as much as 7 per cent. of NH_3, while with a slow gas current 11·9 per cent. of NH_3 is obtainable at 500° with a pressure of 125 atmos. The finely divided osmium is prepared by heating osmyldiammine, but uranium is conveniently used as uranium nitride (action of nitrogen in the hot on uranium), U_3N_4, which is obtained in very fine powder soluble in water.

Practical experience with the Haber process showed that the steel vessels, at high temperatures and pressures and in presence of the gas, developed cracks after long use, but this difficulty was overcome by the use of special steels.

The Badische Company found (Ger. Pats. 249,447, 258,146, and 254,337) that there are substances (*e. g.*, oxides, hydroxides, salts, and certain metals) capable of increasing the activity of certain slow catalysts especially if the activators (even only 1 per cent.) are melted with the catalyst in an oxidising medium and the whole mass then reduced. In such case, it is necessary to exclude—since they act as poisons—phosphorus, arsenic, sulphur, selenium, tellurium, boron, carbon monoxide, etc., whilst lead, zinc, tin, bismuth, and their derivatives are of little value. Bernthsen explains the action of the activators by the fact that, during the fusion they dissolve in the oxidised catalyst and then separate out in the mass during reduction and cooling in the form of very fine particles which prevent the metal from losing, partly or entirely, the catalytic properties at its surface. In any case iron exhibits its maximum catalytic activity if it is highly pure and is prepared in a finely divided state by reducing iron compounds (oxides, etc.) with dry hydrogen at a temperature below 600° (Ger. Pats. 247,852, 256,885, 259,702, and 259,871).

According to Ger. Pats. 246,377, 246,454, 250,377, 259,648, and 259,649, molybdenum as nitride forms an excellent catalyst and is prepared by heating oxygenated molybdenum compounds to 1000° in a current of hydrogen and nitrogen alternately. In order to utilise molybdenum as a catalyst it is indispensable (according to Ger. Pat. 254,006) that the gaseous mixture of $N + H$ be free from oxygen and oxygenated compounds. The Société des Nitrures (Ger. Pat. 250,085 and French Pat. 430,595) claims that zinc accelerates the reaction even at 200°. A distinct catalytic action is shown also by lithium, by carbides of the rare earths (Ger. Pat, 259,872), by cerium nitride, by tungsten and its nitride (Ger. Pats. 254,934,259,647, 259,996, and 260,756) and especially by ruthenium (Ger. Pat. 252,997), with which a concentration of 11–12 per cent. NH_3 is attained even at 450° under a pressure of 100 atmos.; the scarcity of ruthenium in nature is, however, greater than that of osmium (*see above*).

by passing the gases under pressure first outside the vessel in which the reaction takes place, so that the pressures inside and outside are the same. The whole is then surrounded by a very strong casing cooled externally as Kunheim and Co. suggested in a patent (Ger. Pat. 45,523, IV. 12 g.) applied for, but afterwards withdrawn. The arrangement used is shown diagrammatically in Fig. 146. The arrows show the passage of the compressed gases first to the outside and then to the inside of the reaction chamber, and the ammonia formed leaves by the inner coil to be condensed in another coil surrounded by a freezing mixture of alcohol and liquid carbon dioxide. The gases which have not reacted return to the compressor and pass again through the cycle.

In starting up the apparatus, the necessary temperature may be reached—besides electrically—by passing air into the reaction chamber, where it burns with the hydrogen given the heat required for initiating the reaction. As the latter is exothermic, when the apparatus is working regularly, the heat of the reaction is used to heat the gases entering the chamber, so that all heating may be dispensed with (Ger. Pat. 259,870).

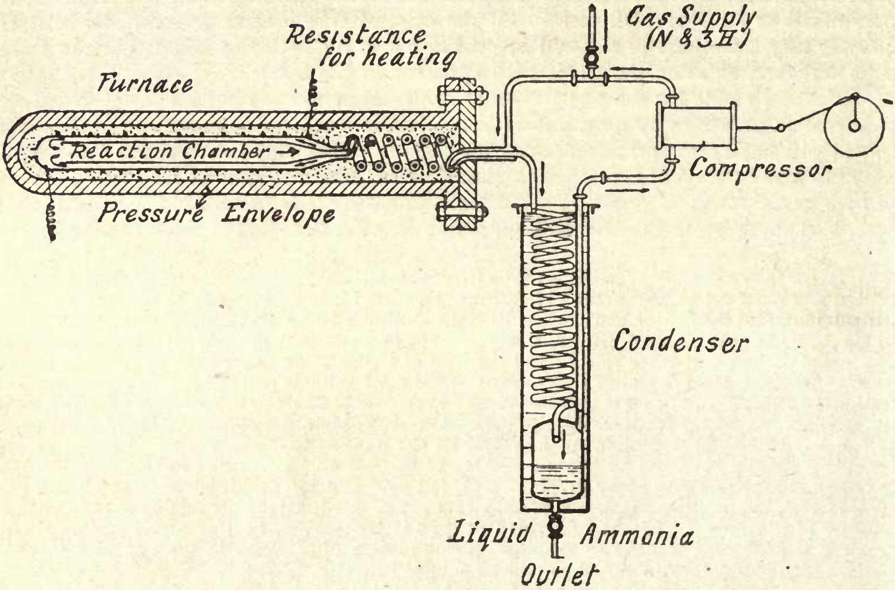


FIG. 146.

Thus, the only mechanical energy necessary in this process is that used for compressing the gases, this being (according to Haber) about 0·5 kilowatt-hour (in some cases 1 kilowatt-hour) per kilo of nitrogen that combines. The cost of synthetic ammonia is made up more especially of the cost of the hydrogen and nitrogen; the former is prepared from water-gas (*see* p. 143) at less than 1·5*d*. per cu. metre (*i. e.*, 1*s*. 7*d*. per kilo), and the nitrogen very cheaply from liquid air—if the maximum value is ascribed to the oxygen, which is nowadays made almost exclusively from liquid air. 100 kilos of ammonia contain 17·6 kilos of hydrogen and 82·4 of nitrogen and, assuming a yield of 90 per cent., about 20 kilos of hydrogen (222 cu. metres) and 90 of nitrogen (66 cu. metres) are required to prepare 100 kilos of ammonia, *i. e.*, 25*s*. 6*d*. for the hydrogen and about 3*s*. 3*d*. for the nitrogen. The cost of compression is considerable since the gases of the reaction contain only 5–8 per cent. of NH_3, so that for 100 kilos of ammonia about 5800 cu. metres of gas must be compressed; the recovered gases have still, however, a high pressure—about three-fourths of the maximum pressure given by the compressor—and for small plants the consumption is about 2 kilowatt-hours per kilo of nitrogen or 164·8 per 100 kilos of ammonia produced, this costing, say, 2*s*. 6*d*. There must also be added the cost of condensing the ammonia, labour, general expenses, sinking fund (on £60,000), cost of patents and repairs and unforeseen expenses, the total for an output of 3000 kilos per twenty-four hours being about 56*s*. per

100 kilos of ammonia; thus the combined ammonia will cost about 8*d.* per kilo, in comparison with about 1*s.* 3*d.* in the case of nitrate or ammonium sulphate.

By the end of 1913 the Badische Anilin und Soda-Fabrik had at work at Oppau near Ludwigshaufen a synthetic ammonia works with a capacity of 100 tons of ammonia per day. The product was sold first in the pure liquefied form and then also as ammonium sulphate in competition with that of the Bochum Syndicate. Later an arrangement was made between the competitors, the sale of liquid ammonia being reserved to the Badische Company.

ANALYTICAL TESTS. The strength is usually determined by means of the density (see Table, p. 354) or by titration with standard acid; when the product is pure it should leave no residue on evaporation in a dish; with HNO_3 and $AgNO_3$ no opalescence due to chlorides should appear, nor should there be any turbidity on neutralising with HCl and adding barium chloride (sulphates); no turbidity should be caused with excess of lime-water (carbonates); 10 c.c., to which 20 c.c. of dilute sulphuric acid (1 : 3) have been added, should remain coloured with one drop of decinormal permanganate (tarry matter). The ammonia in ammoniacal compounds is determined by treating them with excess of sodium hydroxide and distilling in a current of steam. All the ammonia distils and is condensed in a standard solution of acid coloured with methyl orange; the excess of acid is then titrated back with normal soda; 1 c.c. of normal acid corresponds with 0·017 grm. of NH_3.

PURE LIQUID AMMONIA, free from water, is prepared by distilling the concentrated aqueous solution (b. pt. 38°) or by taking the pure gas (*see* p. 360) before condensation. In either case the gas is dried in towers containing quicklime, collecting it in a gasometer with an oil reservoir in which various impurities (N_2O, alcohol, benzene, pyridine, etc.) are separated. At + 10° it can be liquefied under 6·5 atmos. in steel cylinders. The liquefaction is carried out as with sulphur dioxide (*see* p. 280), but is conveniently effected in two phases; in the first, the gas is compressed to 3–4 atmos. (further impurities being thus separated) and then, with cooling to 15–20°, to 8 atmos. The product may be employed in the manufacture of ice. At 0° it has a specific gravity of 0·6233. It boils at — 32·5° and forms a mobile, colourless liquid which solidifies at — 88·3° and then melts at — 78·3°; its critical temperature is + 131°. Liquid ammonia is one of the few substances which have a higher specific heat than water, this being 1·02 between 0° and 20°. Its heat of evaporation is about 300 Cals. per kilo, but varies somewhat with the temperature, being 333 Cals. at — 40° and 278 Cals. at + 40°. The vapour pressure of liquid ammonia at — 40° is 270 grms. per square centimetre; at 0° it is 4350 grms., at 20° 8790 grms., and at 40° 16,000 grms. The requirements demanded of commercial liquid ammonia are: 100 c.c. should leave a residue of less than 0·5 c.c.; 1 grm. of liquid ammonia shall not contain more than 0·12 c.c. of foreign gases in solution; the vapours of NH_3 above the liquid ammonia shall not contain more than 0·6 c.c. of other gases per gram.

A volume of at least 1·86 litres must be allowed per kilo of liquid ammonia.

STATISTICS, APPLICATIONS, AND PRICES OF NH_3. Aqueous commercial ammonia containing about 25 per cent. of NH_3 is used in laundries, dyeworks, textile print works, colour factories, etc. (after dilution), and costs about £20 per ton (£14 for large quantities) or £8 if it contains 10 per cent. of NH_3. The purest aqueous solution costs 20 per cent. more. Liquid ammonia free from water is used in ice factories and costs up to 1*s.* 7*d.* per kilo at the works, exclusive of the hire of the steel cylinders (*see* p. 192); delivered at Milan it costs about 2*s.* 4*d.* per kilo.

In 1909 about 60 tons of liquid ammonia were used in Italy, almost the whole of which was imported from Germany and Belgium in 20 kilo cylinders at about 2*s.* per kilo, a small quantity only being produced in a works at Turin (4 tons in 1908, of the value of £320, and 12 tons in 1914).

In Germany 1500 tons of liquid ammonia were consumed in 1913.

In 1902 Italy imported 79·8 tons of ammonia in solution of the value of £1468, in 1904 only 66·2 tons (£1218), in 1906 129·6 tons, in 1907 121·4 tons, in 1908 146 tons (£2570), in 1914 130 tons, and in 1915 350 tons (£8400). In 1908 Italy produced 16,373 tons of ammonia liquors, valued at £3860, from gas-works and in 1915 55,66 tons; also 150 tons of commercial aqueous ammonia (£1950) in 1908 and 1390 tons (£9144) in 1915. The consumption in Italy in 1911 was estimated at 350 tons.[1]

The output of ammonia in England was as follows: 1910, 367,588 tons; 1911, 384,976 tons; 1912, 388,308 tons — 55 per cent. from gas-works, 25 per cent. from coke furnaces, and 17 per cent. from the distillation of bituminous shale.

OTHER HYDROGENATED AND HALOGENATED DERIVATIVES OF NITROGEN

DIAMINE OR HYDRAZINE, N_2H_4 or $H_2 : N \cdot N : H_2$.

This compound, which appears to be derived from the condensation of 2 mols. of NH_3, was known in the form of many of its organic derivatives long before it had been obtained in the free state; many inorganic derivatives were also prepared by Curtius after 1889, and in 1895 Lobry de Bruyn prepared pure diamine. It is obtained to-day in various ways—by decomposing its hydrochloride with alkyloxides or by distilling its hydrate with barium oxide. It is a colourless liquid which boils at 113·5° and fumes strongly in the air; it has a specific gravity of 1·003 at 23° and solidifies at 0°. It is not explosive and is distinguished from ammonia by its reducing power.

HYDRAZINE HYDRATE: N_2H_4, H_2O, forms an energetic base similar to ammonia but of great reducing power, and readily decomposes silver and copper salts.

AZOIMIDE OR HYDRAZOIC ACID: N_3H, that is,  $\begin{matrix}N\\ \|\\ N\end{matrix}\!\!>NH$. This was first prepared by Curtius in 1890 from the corresponding organic derivatives. He then obtained it from inorganic substances by pouring nitrous acid (liquefied red vapours obtained by the action of arsenious acid on nitric acid) into hydrazine hydrate:

$$H_2N \cdot NH_2 + NO_2H = 2H_2O + N_3H.$$

It is also obtained in aqueous solution by distilling metallic hydrazides with dilute sulphuric acid.

When pure it forms a mobile colourless liquid of very pungent odour, which boils at 37° and explodes with extraordinary violence. It is an endothermic compound, and the heat absorbed in its formation and solution is 260 Kj. The alkali salts are not explosive, but its alkaline earth and other salts explode. Turrentine (1914) attributes to it the formula, $NH : N \vdots N$.

HYDROXYLAMINE: NH_2OH

This compound is a product of the partial reduction of oxy-compounds of nitrogen. It was prepared in 1865 by reducing the organic esters of nitric acid, but was obtained pure and free from water only in 1891. It is formed also by treating nitric acid with tin, or nitrogen oxides with HCl and tin.

Nascent hydrogen reduces nitric acid, nitrates, and nitrogen oxides:

$$NO_3H + 3H_2 = 2H_2O + NH_2OH.$$

Hydroxylamine hydrochloride is easily obtained by treating mercury fulminate ($C_2N_2O_2Hg$) with hydrochloric acid. It forms colourless, odourless crystals, melts at 43° and boils at 58° at reduced pressure (22 mm.).

It is a liquid which is stable below 15°, but at higher temperatures commences to decompose into N, N_2O_3 and NH_3, and at about 130° it explodes.

It is hygroscopic, has basic characters and, like ammonia, forms salts with acids, by direct addition: $NH_3O + HCl = NH_3O, HCl$, hydroxylamine hydrochloride, which is distinguished from ammonium chloride by being soluble in alcohol. The aqueous solution of hydroxylamine acts as a strong reducing agent; for instance, it separates silver from silver nitrate.

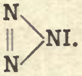
---

[1] The cost of a small plant for the manufacture of 10 cu. metres of aqueous ammonia in twenty-four hours would be about £200 for the distilling apparatus, including the pump for the milk of lime and the pipes. The apparatus for obtaining concentrated aqueous ammonia with 15 per cent. of NH_3 comprises a reflux condenser, two condensing vessels, piping and cocks, and, with erection, costs £200. In order to obtain more concentrated solutions of pure aqueous ammonia, containing 30 per cent. of NH_3, 3 lime-washers, 6 coke filters, and two absorption vessels are required at a cost of about £200.

NITROGEN CHLORIDE, NCl_3. When ammonia reacts with an excess of chlorine, instead of free nitrogen (*see* p. 333), ammonium chloride is first formed, this immediately producing nitrogen chloride: $NH_4Cl + 3Cl_2 = 4HCl + NCl_3$. This chloride is a yellow, oily liquid of disagreeable odour and of sp. gr. 1·65. It is extremely dangerous to handle, and the slightest shock, even rubbing with a feather, suffices to cause a violent explosion, owing to the facility with which it decomposes into its elements. It is decomposed by means of concentrated HCl into the substances from which it is formed, $NCl_3 + 4HCl = 3Cl_2 + NH_4Cl$ (inverse reaction to that of formation).

Aqueous NH_3 also decomposes it slowly, forming $N + NH_4Cl$.

NITROGEN IODIDE, NI_3. If ammonia is added to a solution of iodine in potassium iodide a black powder of NI_2H is first formed and then $N_2I_3H_3$ ($= NI_3 + NH_3$); with much water, this gives NI_3. These compounds are extraordinarily explosive when dry, being exploded even by the slightest friction. HCl, SO_2, and H_2S easily decompose these nitrogen iodides.

IODIDE OF AZOIMIDE (or **TRIAZOIODIDE**),  $\overset{N}{\underset{N}{\|}}\!\!>\!NI$. This compound, which was first prepared in 1900, appears to be a derivative of hydrazoic acid and is, in fact, obtained by the action of silver azide on iodine in ethereal solution in the cold: $N_3Ag + I_2 = AgI + N_3I$.

It forms a bright-yellow solid substance which already decomposes with water and is also very explosive.

The great instability and explosibility of the halogen compounds of nitrogen are explained by the fact that they are strongly *endothermic*.

OXYGEN COMPOUNDS OF NITROGEN

Nitrous Oxide, N_2O, with which, by the addition of 1 mol. of water, 2 mols. of hyponitrous acid, $NO \cdot H$, correspond.

Nitric Oxide, NO, which has no corresponding acid.

Nitrogen Trioxide or **Nitrous Anhydride**, N_2O_3 or $O : N \cdot O \cdot N : O$, which yields 2 mols. of nitrous acid, HNO_2, with H_2O.

Nitrogen Dioxide (or peroxide), NO_2, and **Nitrogen Tetroxide**, N_2O_4, which may be considered as mixed anhydrides of nitrous and nitric acids.

Nitrogen Pentoxide or **Nitric Anhydride**, N_2O_5, which forms nitric acid, NO_3H, with water.

It is thought by some that the oxide, NO_3 (? hexoxide), exists.

The formation of these oxides from the elements is endothermic:

$$\begin{aligned}
2N_2 + O_2 &= 2N_2O && - 2 \times 20600 \text{ cals.}\\
N_2 + O_2 &= 2NO && - 2 \times 21500 \quad ,,\\
2N_2 + 3O_2 &= 2N_2O_3 && - 2 \times 21400 \quad ,,\\
N_2 + 2O_2 &= 2NO_2 && - 2 \times 7600 \quad ,,\\
2N_2 + 5O_2 &= 2N_2O_5 && - 2 \times 1200 \quad ,,
\end{aligned}$$

NITROUS OXIDE: N_2O

This compound is easily obtained by heating ammonium nitrate to above 100°, $NO_3NH_4 = 2H_2O + N_2O$; towards 240° the reaction becomes tumultuous and even explosive, so that it is preferable to heat a mixture of sodium nitrate and ammonium sulphate to 230° in a cast-iron retort.

The gas is evolved regularly and may be collected in a gas-holder over mercury, hot water (in cold water it dissolves to some extent), or saturated salt solution.

When it is to be compressed in steel cylinders for use as an anæsthetic, it is freed from other oxides of nitrogen (NO) and from chlorine by passing it successively through water, ferrous sulphate solution, and caustic soda solution. It is then cooled to − 60° (with a mixture of liquid SO_2 and CO_2) to free it from water, a pressure of 12–14 atmos. then sufficing to liquefy it in steel cylinders (previously tested to 250 atmos.). From 100 kilos of ammonium nitrate about 40 kilos of N_2O (90 per cent. of the theoretical yield) are obtained.

The formation of N_2O from an isomeride of ammonium nitrate, namely, hydroxylamine nitrite, which already gives N_2O in aqueous solution, is of interest: $NO_2H, NH_2OH = 2H_2O + N_2O$.

It is also formed, together with NO, by treating zinc and tin with nitric acid of sp. gr. 1·1; also by the action of moistened iron filings on NO, and was thus obtained for the first time by Priestley in 1772, together with iron oxide.

Quartaroli (1911) obtained it in quantitative yield by heating formic acid with various nitrates, the CO_2 formed at the same time being absorbed by means of caustic soda.

Nitrous oxide is a colourless gas of a sweetish taste; 1 litre weighs 1·97 grms. and 1 vol. of water at 0° dissolves 1·3 vols. of the gas; it is still more soluble in alcohol. By pressure and cooling it is transformed into a colourless mobile liquid, which boils at — 87·9°, and when allowed to evaporate rapidly, this solidifies at — 102° to a white crystalline mass.

The sp. gr. of the liquid varies greatly with the temperature; at 16·5° it is 0·817, at 27° 0·725, and at 33° 0·656. The vapour pressure of the liquid is 50 atmos. at 15°. The critical temperature is 35·4° and the critical pressure 75 atmos. The heat of evaporation at 0° is 59·5 Cals. It is a stable gas and begins to dissociate only above 520°.

It maintains and revives the combustion of phosphorus, wood, etc., more easily than nitric oxide, in spite of the fact that it contains less oxygen, because it is less stable and immediately liberates the oxygen which it contains.

With an equal volume of hydrogen it forms an explosive mixture, and although in many respects it behaves similarly to oxygen it may be distinguished from the latter gas, as it does not combine with NO, whilst oxygen and NO together form reddish-brown vapours of NO_2 and N_2O_3; it does not combine with oxygen, by which means it is easily distinguished from NO. When inspired in small doses it produces a form of inebriation, so that it has also been called "laughing gas." When inspired pure or mixed with 1 vol. of oxygen it acts as an anæsthetic and is used in surgery (proposed by Wells, 1840), especially by dentists.

It is an endothermic compound and absorbs 75 Kj during its formation.

HYPONITROUS ACID : $H_2N_2O_2$

This compound has been discovered during the last few years and is supposed to be derived from N_2O and H_2O; such reaction, however, has not yet been effected, although N_2O has been obtained by abstracting water from hyponitrous acid obtained by other means.

It is prepared in various ways—by reducing nitric or nitrous acid or by oxidation of hydroxylamine. Thus, for example, on reducing potassium nitrite with sodium amalgam, potassium hyponitrite is formed; the sodium hydroxide formed by the amalgam is neutralised with acetic acid and the hyponitrous acid separated by means of silver nitrate as yellow, solid, amorphous, silver hyponitrite, which is decomposed with HCl. The hyponitrous acid so liberated is extracted with ether and the ethereal solution then evaporated *in vacuo*, when a scaly, crystalline, unstable mass of free hyponitrous acid remains. It explodes easily, and in contact with solid sodium hydroxide catches fire; it is hygroscopic and soluble in alcohol, ether, and chloroform. It is slowly transformed in aqueous solution into $N_2O + H_2O$.

It separates iodine from potassium iodide and decolorises potassium permanganate, being transformed into nitric acid.

NITRIC OXIDE: NO

This compound was first studied by Priestley in 1772. It is not found free in nature because it combines readily with oxygen, forming nitrogen dioxide. It is formed from its elements at temperatures above 1200°, and industrially by the action of the electric discharge in air (*see* p. 391), but the gaseous mixture which results does not contain more than 1·5 per cent. of NO (for the conditions of the equilibrium and dissociation, *see* p. 392).

Fischer (1913) showed that if oxygen is subjected to the action of the electric discharge it becomes capable of combining immediately with nitrogen, forming NO,[1] whilst the similar dissociation of nitrogen observed by Strutt is without influence on the combination.

It is also formed when various metals are dissolved in dilute nitric acid. Thus, it may be obtained by treating copper turnings with nitric acid of sp. gr. 1·2, or by dropping concentrated sulphuric acid (400 grms.) on to a mixture of copper turnings (60 grms.) and sodium nitrate solution (800 grms.), but the yield is low: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$.

A regular evolution of the gas is obtained from mercury with strong sulphuric acid to which 2 per cent. of sodium nitrite or nitrate has been added.[2]

When all the air in the apparatus has been displaced red vapours of NO_2 are no longer formed, but only colourless NO, which may be collected in a cylinder by displacement of water. The gas is obtained pure from a mixture of potassium nitrite, yellow prussiate of potash and acetic acid. It is produced more conveniently, abundantly, and economically by Schlösing's reaction: 100 grms. of concentrated sodium nitrate solution (containing 45 grms. of the salt) is dropped into a flask (on a water-bath) containing 425 grms. of ferrous sulphate and 445 grms. of sulphuric acid of 52° Bé. (yield almost theoretical: Molinari, 1910).

Nitric oxide is a colourless gas, only slightly soluble in water, but more soluble in solutions of ferrous chloride or sulphate, which are coloured reddish-brown thereby; from these solutions it is again evolved in a purified condition on heating. It dissolves also in nitric acid, forming brown, yellow, green, or blue solutions according to the concentration. With pure HNO_3 it forms nitrous anhydride, N_2O_3; it is insoluble in sulphuric acid (*see* Gay-Lussac Tower, p. 300). The constitution of nitric oxide is determined from the fact that when a given volume of it is treated with sodium, Na_2O and N_2 are formed, the latter gas occupying half the space which was at first occupied by the NO.

One litre of the gas weighs 1·3426 grms. It is liquefied only at − 154°, and is solid at − 167°. It is transformed by potassium permanganate into nitric acid. It maintains the combustion of substances which evolve much heat on oxidation (for example, phosphorus, but not sulphur). When mixed with carbon disulphide vapours it burns with an intense blue flame very rich in actinic rays.

It is a strongly endothermic compound (— 90 Kj. = — 21,500 cals.), and this explains the fact that its molecules are more unstable than those of oxygen, so that on burning substances (such as P and C) in an atmosphere of NO 21,500 cals. more are evolved than on burning the same substances in oxygen; in order to dissociate the atoms of the oxygen molecule more heat is therefore required than to dissociate the molecule of NO (*see* Manufacture of Nitric Acid from Atmospheric Nitrogen).

By means of sufficient oxygen it is immediately and completely transformed into nitrogen dioxide: 2 vols. NO + 1 vol. O_2 = 2 vols. NO_2.

When a deficiency of oxygen is present nitrous anhydride, N_2O_3, is formed.

[1] This is due probably to dissociation of the diatomic molecules into monatomic molecules of oxygen which are much the more active. The thermal effects and velocity constants for the reaction, $N_2 + 2O = 2NO$, differ considerably from those of the reaction, $N_2 + O_2 = 2NO$. Taking for the dissociation of O_2 an absorption of 26,320 cals. and for the endothermic formation of NO an absorption of 21,500 cals. (*see later*), we have $N_2 + 2O = 2NO + 26,320 - 2 \times 21,500$ cals. $= 2NO - 2 \times 8,340$ cals. and the absolute value of $\frac{d \log k}{dt}$ (*see* notes, pp. 390, 392) will be less than that for the reaction, $N_2 + O_2 = 2NO$.

[2] This reaction is used for the analysis of sodium nitrate, mixtures of nitric and sulphuric acids, and "nitrous" acids by means of the nitrometer, NO being liberated by treatment with mercury and the gas formed measured (*see* nitrometer): $2HNO_3 + 6Hg + 3H_2SO_4 = 4H_2O + 3Hg_2SO_4 + 2NO$.

With chlorine and bromine it forms nitrosyl chloride, NOCl, and nitrosyl bromide, NOBr (*see below*).

Nitric oxide may be easily separated from other gases, such as N_2O, CO, CO_2, N_2, etc., by adding a little oxygen to the mixture so as to transform the NO into N_2O_3 and fixing this with a little ethylaniline.

At a red heat it forms NO_2 and N. It burns with hydrogen on heating, forming a greenish flame: $NO + H_2 = N + H_2O$. In presence of spongy platinum, on the other hand, it forms NH_3.

NITROSYL CHLORIDE, NOCl, is now used industrially for bleaching, especially for bleaching wheaten flour, according to Wesener's patent (Ger. Pats. 209,550 of 1908 and 232,204 of 1910); its preparation has been suggested in various ways: *e. g.*, by passing a current of 2 vols. of NO and 1 vol. of Cl over bone-black at 60° (Francesconi and Bresciani, 1904), but it is difficult to obtain a good yield, and moreover, combination also occurs to some extent in the cold and in absence of the charcoal. It may be obtained by treating nitrosylsulphuric acid with sulphuric and nitric acids in presence of sodium chloride, or from nitric acid and dry sodium chloride with strong sulphuric acid; Cl and NOCl are evolved and the latter is condensed by means of ice and salt. More convenient industrially is the direct union of about 2 vols. of dry NO with 1 vol. of moist Cl in a large bottle filled with lumps of lime and cooled externally; the gases evolved are dried with fused calcium chloride (lumps) and the NOCl liquefied in a leaden coil cooled, as is also the collecting vessel, to − 12° (Molinari, 1910). It is conveniently prepared on a large scale by the direct combination of liquid NO and liquid Cl in the theoretical quantities; the mutual solution of the two compressed and cooled liquids is instantaneous (Fenaroli, 1911). It is a gas of brownish-orange colour which forms an orange-red liquid on cooling. This liquid boils between − 8° and − 6°, and solidifies at − 65°, forming crystals of a blood-red colour. It is easily decomposed by water. With sulphuric acid it forms nitrosylsulphuric and hydrochloric acids; it colours the skin yellow in the same way as strong nitric acid. With 1 kilo of nitrosyl chloride, diluted with a large quantity of air, 100 tons of flour may be bleached. This use of nitrosyl chloride became widespread in the United States, and was also introduced into France and Italy. For several reasons, however, this process has been abandoned in Italy and in some other countries; a mixture of liquid chlorine with 5 per cent. of nitrosyl chloride (Ger. Pat. 267,972, 1912) is now employed. Liquid nitrosyl chloride in steel cylinders costs 9*s*. 6*d*. to 11*s*. per kilo.

NITROGEN TRIOXIDE (NITROUS ANHYDRIDE), N_2O_3

This gas is obtained from NO with a limited quantity of oxygen at − 18°: $2NO + O = N_2O_3$; also by saturating liquid nitrogen tetroxide with NO: $N_2O_4 + 2NO = 2N_2O_3$, or by passing NO into pure concentrated cold nitric acid. Helbig obtained it in the solid state in bluish-green flocks by passing the electric arc through liquid air, but Scarpa (1907) showed that in this case NO is first formed and then diffuses into the liquid air and unites with the oxygen to form N_2O_3; the latter melts at − 111° and afterwards undergoes partial decomposition.

It is conveniently prepared by heating nitric acid of sp. gr. 1·25 with starch or arsenious anhydride on the water-bath in a flask with a delivery tube, and condensing the vapours formed in a U-tube surrounded by ice:

$$As_2O_3 + 2NO_3H + 2H_2O = 2AsO_4H_3 + N_2O_3.$$

It is always formed when nitrates are heated with strong sulphuric acid at high temperatures.

N_2O_3 is fairly stable at − 21° and forms a blue liquid (of sp. gr. 1·44 at 0°), which boils at − 3·5° and gradually decomposes, forming brown vapours: $N_2O_3 = NO_2 + NO$. These two gases re-form N_2O_3 in the cold; at a red heat it forms NO and also N. Whether N_2O_3 is a true chemical compound or a mixture of NO_2 and NO has been under discussion for some years; Lunge regards it as an actual compound, which is completely dissociated at 150°.

With H_2SO_4 it forms nitrosylsulphuric acid which is immediately decomposed by water, forming nitrous fumes and sulphuric acid, as occurs in the lead chamber (*see* p. 288).

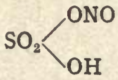
With a little cold water and still more readily with much hot water it is slowly decomposed, forming HNO_3 and NO. A fresh aqueous solution of N_2O_3 is stable, but *does not show the reactions of nitrous acid*; by hydrogen peroxide it is quantitatively transformed into nitric acid, whilst it is not completely oxidised by permanganate. Amyl acetate dissolves 20 per cent. of it.

NITROUS ACID: HNO_2

This compound is not known free, but only in the form of its salts, called *nitrites*, which are obtained by heating nitrates to redness: $NO_3K = NO_2K + O$; the reaction is facilitated by the addition of oxidisable metals such as lead. The nitrites give brown vapours of $NO_2 + NO$ with sulphuric acid.

Nitrous acid is supposed to exist free in aqueous solution. It is a strong oxidising agent and separates iodine from iodides, transforms sulphurous into sulphuric acid, ferrous sulphate into ferric sulphate, and yellow potassium ferrocyanide into the red ferricyanide. Sometimes, however, it acts as a reducing agent; thus, it decolorises violet solutions of potassium permanganate, being transformed into HNO_3. This reaction in dilute solution occurs quantitatively both for nitrous acid and for nitrites in presence of sulphuric acid, and on it is based a quantitative method of analysing commercial nitrites. The end of the reaction is indicated by the disappearance of the violet colour:

$$5NO_2H + 2MnO_4K + 3SO_4H_2 = 5NO_3H + SO_4K_2 + 2SO_4Mn + 3H_2O.$$



NITROSYLSULPHURIC ACID, $SO_2\langle^{ONO}_{OH}$ (or NITROSOSULPHURIC ACID)

This acid has already been described in connection with the preparation of sulphuric acid (*see* p. 288), and forms the well-known lead chamber crystals; when dissolved in sulphuric acid it forms the so-called nitrous sulphuric acid. Mercury and also sulphur dioxide liberate NO from this acid, and this explains the denitrifying action of the SO_2 in the Glover tower during sulphuric acid manufacture. It is always formed when nitrogen oxides (excepting N_2O) come into contact with sulphuric acid; it is easily prepared by passing pure sulphur dioxide in the cold into fuming nitric acid until the latter is saturated, a crystalline mass of nitrosylsulphuric acid then separating. The pure crystals melt at 73°, being transformed into the anhydride, $S_2O_5(NO_2)_2$. It is decomposed by water into sulphuric acid and nitrous fumes; it is soluble in sulphuric acid, its solubility increasing with concentration of the acid, the solution being colourless in the cold and yellow when hot. It is stable at high temperatures when the acid in which it is dissolved has a concentration greater than 60° Bé.

NITROGEN PEROXIDE, $(NO_2)_x$; NITROGEN TETROXIDE, N_2O_4; and NITROGEN DIOXIDE, NO_2

When the electric arc is passed through a mixture of dry oxygen and nitrogen, NO is first formed, and this with sufficient oxygen from the air is transformed into NO_2 (for conditions of its formation, *see* Synthetic Nitric Acid).

It is conveniently prepared by heating dry lead nitrate:

$$(NO_3)_2Pb = PbO + O + 2NO_2;$$

the oxygen is then separated from the reddish-brown vapours of NO_2 by cooling below 0° until the latter are liquefied; a yellowish liquid formed of N_2O_4 is thus obtained.

The tetroxide, N_2O_4, is stable only below 0°; at higher temperatures it gradually dissociates, forming NO_2, and at 150° the transformation into NO_2 is complete, as may be easily deduced from the gradual diminution in the vapour density with rise of temperature. On again cooling at 0° the gaseous tetroxide, which is only very slightly coloured, is re-formed, whilst the gaseous dioxide has a red-brown colour.[1] At $-20°$ the tetroxide forms a white crystalline mass which melts at from $-10°$ to $-12°$. Above 0° the liquid acquires a brownish-yellow colour and boils at 26°, forming red-brown vapours which steadily become darker with elevation of the temperature and consequent increase in the amount of NO_2. Amyl acetate dissolves 20 per cent. of NO_2.

With a little very cold water nitrogen tetroxide, N_2O_4, forms nitric acid and nitrous anhydride, which colours the liquid blue:

$$2N_2O_4 + H_2O = N_2O_3 + 2NO_3H;$$

with excess of cold water colourless nitric and nitrous acids are formed: $N_2O_4 + H_2O = NO_3H + NO_2H$, showing that nitrogen tetroxide is simply a mixed anhydride of nitric and nitrous acids, $NO_2 - O - NO$ (analogous to chlorine tetroxide).

If hot water is used instead of cold water the nitrous acid is decomposed and evolves NO, whilst nitric acid remains: $3NO_2H = H_2O + NO_3H + 2NO$.

It is an energetic oxidising agent, maintaining combustion and separating iodine from soluble iodides. It differs from NO in not being very soluble in water, or even in sulphuric acid. Even when it is diluted with much air, wood charcoal absorbs it with great avidity, and it may be liberated from the carbon by means of steam. Metals which have been recently reduced with hydrogen, for instance, copper, absorb up to 1000 vols. of N_2O_4, forming *nitro-metals* (Cu_2NO_2).

During the formation of NO_2 heat is absorbed (— 5260 cals., or 22 Kj.), whilst during the formation of N_2O_4 from NO_2 heat is developed (12,900 cals., or 54 Kj.).

NITROGEN PENTOXIDE, N_2O_5 (NITRIC ANHYDRIDE)

This is the most highly oxidised compound of nitrogen, and is obtained, together with metaphosphoric acid, by heating a mixture of nitric acid and phosphorus pentoxide to a moderate temperature in a retort: $2NO_3H + P_2O_5 = N_2O_5 + 2PO_3H$.

The distillate condenses as a solid in a flask cooled with ice.

It is obtained pure by the action of perfectly dry chlorine on dry silver nitrate, $2NO_2OAg + 2Cl = NO_2ONO_2 + 2AgCl + O$.

Nitrogen pentoxide forms prismatic crystals of the rhombohedral system, melting at 30° and boiling at 47°. It decomposes easily, even with spontaneous explosion, and readily forms nitrogen tetroxide, N_2O_4, and O. By water it is immediately transformed into nitric acid with evolution of heat: $N_2O_5 + H_2O = 2NO_3H$. The heat of formation of

---

[1] The equilibrium conditions between NO_2 and N_2O_5 at various temperatures are as follows (Deville and Troost):

At	26·7°	20·00 %	NO_2	and	80·00 %	N_2O_4.
„	60·2°	50·04 %	„	„	49·96 %	„
„	100·1°	89·23 %	„	„	10·77 %	„
„	140°	100 %	„	„	0 %	„

gaseous N_2O_5 is zero. When it passes into the solid state 55 Kj. are evolved, and dissolution in water yields a further 70 Kj. (16,750 cals.).

NITRIC ACID: HNO_3

This compound is rarely found free in nature, but is, on the other hand, abundant in the form of salts, such as calcium, ammonium, and potassium nitrates, and especially sodium nitrate (Chili Saltpetre, *see* Part III), in regions with very low rainfall, such as Peru, Chili, and Bolivia. It is sometimes formed in minimal quantities by the action of electrical discharges on moist air, but more easily in the presence of NaOH, when sodium nitrate is formed; it is formed in the soil through the oxidation of ammonia and ammonium salts.

HNO_3 is prepared in laboratories by distilling sodium or potassium nitrate with strong sulphuric acid in a retort, and collecting the nitric acid which distils in a glass flask cooled in a stream of cold water; the acid sulphate of sodium or potassium remains in the retort:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + NO_3H.$$

This reaction occurs at a temperature of about 130°, but if this temperature is much exceeded (above 200°) the acid sulphate can be converted into neutral sodium sulphate, so that a single molecule of H_2SO_4 is then able to decompose 2 mols. of the nitrate. The nitric acid formed at this temperature is, however, decomposed into $NO_2 + H_2O + O$ and the NO_2 dissolves in the nitric acid which is first formed so that an acid of yellow-brown colour, called *fuming nitric acid*, is produced.

Until 1855 potassium nitrate was used technically for the manufacture of HNO_3 instead of sodium nitrate, in spite of the fact that the former was dearer, because potassium nitrate crystallises the more easily, and is therefore the more easily obtained pure, so that a purer acid was formed.

Since 1855, however, the improvements introduced into the purification of sodium nitrate (Chili saltpetre) have made it possible to obtain this salt in a very pure crystallised condition, and from that time it has been adopted exclusively in the nitric acid industry.

PROPERTIES. Nitric acid completely free from water has not yet been obtained, but concentrations of 99·8 per cent. of HNO_3 (stable at 0°) have been reached. This acid is colourless and fumes in the air. It has a specific gravity of 1·56, and solidifies at − 47° to a crystalline mass; it decomposes at relatively low temperatures, especially in direct sunlight, then acquiring a brownish-yellow colour through the formation of NO_2. It commences to boil at 86° and is decomposed to a small extent, so that the first portions which distil are yellowish, whilst afterwards the distillate is colourless but contains a little water.

The vapours are decomposed at 260°: $2NO_3H = 2NO_2 + H_2O + O$.[1]

It is extremely soluble in water, and on distilling dilute nitric acid water first passes over; then at 121° an acid containing 68 per cent. of HNO_3 and of sp. gr. 1·414 (42° Bé.) distils, and this forms the concentrated nitric acid of commerce. If this acid is distilled with five parts of strong sulphuric acid, pure nitric acid almost free from water is obtained, and on passing a current of air through this acid a little NO_2 which remains in solution is liberated.

---

[1] The increase in the decomposition of nitric acid with rise of temperature is as follows:

At 86°,	9·53 % is decomposed.
,, 100°,	11·77 % ,,
,, 130°,	18·79 % ,,
,, 160°,	28·96 % ,,
At 190°,	49·34 % is decomposed.
,, 220°,	72·07 % ,,
,, 250°,	93·03 % ,,
,, 256°,	100 % ,,

We give a Table of the various concentrations of nitric acid, but this does not apply to fuming (yellow) nitric acid, because the dissolved N_2O_4 increases the specific gravity in a very irregular manner:

Sp. gr. at $\frac{15^\circ}{4^\circ}$ (vacuum)	Degrees Baumé	100 grams contain grms. of HNO_3	1 litre contains kilos of HNO_3	Sp. gr. at $\frac{15^\circ}{4^\circ}$ (vacuum)	Degrees Baumé	100 grams contain grms. of HNO_3	1 litre contains kilos of HNO_3
1·005	0·7	1·00	0·010	1·305	33·7	48·26	0·630
1·015	2·1	2·80	0·028	1·315	34·6	49·89	0·656
1·025	3·4	4·60	0·047	1·325	35·4	51·53	0·683
1·035	4·7	6·37	0·066	1·335	36·2	53·22	0·710
1·045	6·0	8·13	0·085	1·345	37·0	54·93	0·739
1·055	7·4	9·84	0·104	1·355	37·8	56·66	0·768
1·065	8·7	11·51	0·123	1·365	38·6	58·48	0·798
1·075	10·0	13·15	0·141	1·375	39·4	60·30	0·826
1·085	11·2	14·74	0·160	1·385	40·1	62·24	0·862
1·095	12·4	16·32	0·179	1·395	40·8	64·25	0·896
1·105	13·6	17·89	0·198	1·405	41·6	66·40	0·933
1·115	14·9	19·45	0·217	1·415	42·3	68·63	0·971
1·125	16·0	21·00	0·236	1·425	43·1	70·98	1·011
1·135	17·1	22·54	0·256	1·435	43·8	73·39	1·053
1·145	18·3	24·08	0·276	1·445	44·4	75·98	1·098
1·155	19·3	25·60	0·296	1·455	45·1	78·60	1·144
1·165	20·3	27·12	0·316	1·465	45·8	81·42	1·193
1·175	21·4	28·63	0·336	1·475	46·4	84·45	1·246
1·185	22·5	30·13	0·357	1·485	47·1	87·70	1·302
1·195	23·5	31·62	0·378	1·495	47·8	91·60	1·369
1·205	24·5	33·09	0·399	1·501	48·2	94·60	1·420
1·215	25·5	34·55	0·420	1·503	48·3	95·55	1·436
1·225	26·4	36·03	0·441	1·505	48·4	96·39	1·451
1·235	27·4	37·53	0·463	1·507	48·5	97·13	1·464
1·245	28·4	39·05	0·486	1·509	48·6	97·84	1·476
1·255	29·3	40·58	0·509	1·511	48·8	98·32	1·486
1·265	30·2	42·10	0·533	1·513	48·9	98·73	1·494
1·275	31·1	43·64	0·556	1·515	49·0	99·07	1·501
1·285	32·0	45·18	0·581	1·517	49·2	99·34	1·507
1·295	32·8	46·72	0·605	1·520	49·4	99·67	1·515

In aqueous solution nitric acid is almost completely decomposed into the monovalent ions NO_3' and $H^{\cdot}$. It is an energetic acid and oxidises and dissolves almost all metals excepting platinum and gold. Ag, Cu, and Hg are dissolved on heating, but only in presence of NO, though traces of this gas suffice. It transforms almost all non-metals into the corresponding oxy-acids.

It is a strong oxidising agent which attacks organic substances, its action being explained by the following equations: $2HNO_3 = H_2O + N_2O_5$ and $N_2O_5 = 2NO + 3O$. If turpentine is added to a mixture of nitric acid with a little sulphuric acid, it catches fire; also, if resinous coal is ignited it continues to burn if immersed in concentrated nitric acid. The acid transforms benzene directly into nitrobenzene, which is an artificial substitute for bitter almond oil. (This occurs only in presence of strong sulphuric acid.—*Translator's note.*) Boiling HNO_3 transforms sulphur into H_2SO_4.

It oxidises wool and skin, colouring them yellow. It decolorises indigo, forming lower nitrogen oxides (NO and NO_2). Many metals, for example, zinc, are dissolved by dilute nitric acid without evolution of hydrogen, because the latter reduces the nitric acid to ammonia when in the nascent state; in the solution ammonium nitrate is then found together with the metallic nitrate:

$$2NO_3H + Zn = Zn(NO_3)_2 + H_2.$$
$$2NO_3H + 4H_2 = NO_3 \cdot NH_4 + 3H_2O.$$

If, on the other hand, the nitric acid is more concentrated and contains above 10 per cent. of HNO_3, then N_2O, N_2O_3, and N_2O_4 are formed instead of NH_3.

The transformation of nitric acid and of nitrates into NH_3 occurs still more easily in alkaline solution (in presence of NaOH) with the nascent hydrogen produced from zinc dust, iron filings, etc. Tin dissolves in nitric acid with formation of ammonia and also of hydroxylamine.

Nitric acid is monobasic and forms salts called *nitrates*, which are all soluble in water.

INDUSTRIAL MANUFACTURE OF NITRIC ACID. The following advantages are obtained by employing sodium nitrate instead of potassium nitrate: Sodium nitrate costs less than half as much as the corresponding potassium salt, and the same weight produces about 20 per cent. more nitric acid, because the molecular weight of the potassium nitrate is the higher; the sodium bisulphate which is formed in the first phase of the reaction is more easily decomposed than potassium bisulphate, so that the second phase of the reaction occurs at a lower temperature and there is less decomposition of the nitric acid.

In practice, however, it is not found convenient to carry the reaction to the second phase, and it is found preferable to remain at the stage of bisulphate even if this has little or no value.[1]

The glass retorts which were once used have now been completely abandoned and were first replaced by cylindrical, horizontal cast-iron retorts arranged in a furnace with direct flame, and charged with 75 kilos of sodium nitrate and 80 kilos of sulphuric acid of 60° Bé. The nitric acid which was evolved as vapour was condensed in a series of special vessels described later.

In France large cast-iron pots were used by preference, with an almost vertical delivery tube reaching to the bottom in order to remove the molten bisulphate; they first had a capacity of 250 kilos of nitrate, but it was then found more convenient to increase the capacity until they could take a charge of 600 kilos of nitrate and 660 kilos of sulphuric acid of 66° Bé.

Both in the cylindrical retorts and in these cast-iron pots the heat of the furnaces was badly utilised, and as much as 40 kilos of coal were used per 100 kilos of nitrate. The distillation lasted from 15 to 20 hours. Valentiner introduced important improvements in the whole apparatus used in nitric acid factories; he introduced retorts of the shape

---

[1] The quantity of sulphuric acid (calculated as H_2SO_4) to be used is established on the basis of the analysis of the nitrate (a little sodium chloride always present yields HCl even in the cold) and of the strength of the acid itself (use is made of 93–94 per cent. acid, or, if highly concentrated nitric acid is required, even stronger acid). Usually, however, a little less sulphuric acid is taken than is required for the first stage of the reaction, the heating being finally carried so far as to start the second phase, the reason for this being as follows: sodium bisulphate exhibits its maximum fluidity at 160–170°, but liberates all the nitric acid only beyond 240–250°. Increased addition of sulphuric acid is of no avail and is even harmful, since when a mixture of pure sulphuric and nitric acids is distilled, highly concentrated nitric acid first passes over, then more dilute nitric acid, next a mixture of the two acids, and afterwards pure sulphuric acid free from any trace of nitric acid; only when the temperature is raised still more does a mixture of sulphuric acid and oxides of nitrogen distil over. The residue in the retort is yellowish and still contains nitro-compounds, addition of water resulting in evolution of colourless NO, which is oxidised to brown vapours of NO_2 in the air. In nitric acid works, an attempt is made to obtain, not the pure bisulphate ($NaHSO_4$) with an acidity of 40·8 per cent. (as H_2SO_4), but a mixture of the bisulphate and the normal sulphate with an acidity of 36–38 per cent. If, however, too little sulphuric acid is used and the final heating is excessive (beyond 250°), too little sulphate is formed and the residue is insufficiently fluid, so that it is discharged from the retorts only with great difficulty.

indicated in section and plan in Fig. 147, which hold a charge of as much as 1 ton or even 2 tons of nitrate, and applied vacuum distillation to increase the yield with a diminished consumption of fuel and to lessen the decomposition of the nitric acid in consequence of the lower temperature maintained. These large retorts are cast in two pieces, which are joined with flanges and asbestos packing tightened by bolts.

The upper tube which leads away the nitric acid vapours is simply screwed on to the still-head, and may thus be easily changed when corroded without having to change the whole pot. The HNO_3 vapours, instead of passing directly into the battery of condensers, first traverse a small condensing vessel where the salts which are carried over and the froth often formed on working with sulphuric acid of 66° Bé. are separated. When working with acid of 60° Bé., less froth is formed.[1] With this apparatus a purer acid is obtained; the consumption of coal is reduced to 20 kilos per 100 kilos of nitrate and the duration of the process is only 12 hours.

In 1902 Valentiner and Schwarz (Ger. Pat. 144,633) introduced notable improvements which allowed the most concentrated nitric acid (96–98 per cent.) and very pure, to be obtained in a single operation, without the formation of froth, by the use of sulphuric acid of 66° Bé. Instead of adding all the sulphuric acid at once they pass it on to the nitrate (dry) a little at a time, dividing it in a suitable vessel before passing it into the retort; the nitric acid vapours which are gradually evolved are also passed into a vessel where they are washed with concentrated sulphuric acid, which retains the impurities, nitrous fumes, and steam. The vapours which escape from this vessel are pure and very concentrated.[2]

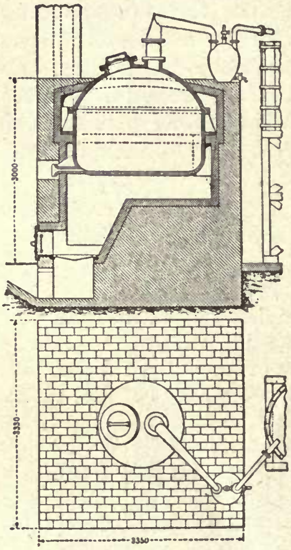


FIG. 147.

CONTINUOUS PROCESSES. Prentice devised an apparatus for the automatic and continuous charging and discharging of the retort, but practical tests made at Stowmarket did not give good results, so that, when the patent lapsed (1898), it was not renewed. H. Schellhass (Ger. Pat. 241,711, 1911) also suggested a continuous process, powdered fused nitrate and atomised sulphuric acid being introduced into heated, vertical, cylindrical retorts.

According to French Pat. 406,969 (1909), a marked advantage attends the use of a continuous distillation process, five retorts being arranged at different levels and the mixture of nitrate and sulphuric acid passed continuously through syphons from each retort to the next. The first retort is heated at 110–120° and gives 60 per cent. of the total acid at a concentration of 96–97 per cent. HNO_3; the second, at 150–170°, yields a 88–90 per cent. acid; the third, at 220–250°, gives a 60 per cent. acid; the fourth, at 260–280°, yields a 15 per cent. acid, and the fifth, at 280–300°, gives an acid of 3·5 per cent. concentration and continuously discharges pure, fused sodium

---

[1] Froth is sometimes formed at the beginning of the distillation when the retort is heated too rapidly, but more commonly appears suddenly towards the end, when the temperature rises too rapidly above 150°, because then all the water combined with the bisulphate ($3H_2O$) is liberated instantaneously, together with part of the residual oxides of nitrogen, producing a pressure in some cases great enough to lift the cover of the pot if the latter is more than half full.

[2] The highest concentration of the nitric acid is obtained by slow distillation at a comparatively low temperature; otherwise less concentrated acid is obtained, even if dry nitrate and the most concentrated sulphuric acid are used. At temperatures somewhat above 86°, nitric acid is decomposed, thus: $2HNO_3 \rightleftharpoons 2NO_2 + O + H_2O$, but at 122°, whilst 15 per cent. of the acid undergoes decomposition, a hydrate of nitric acid (with 32 per cent. of water) may be formed which gives dilute acid on condensation. If the temperature is kept fairly low, concentrated nitric acid may be obtained even if comparatively dilute sulphuric acid is used, since the water formed is fixed by the sodium bisulphate, forming a hydrate which decomposes only at 150°, *i. e.*, at a higher temperature than dilute nitric acid. The above reaction being reversible, the decomposition of the nitric acid may be diminished by injection of a small jet of air into the delivery tube of the retort before the condensation battery is reached (*see* right-hand side of Guttmann and Rohrmann's apparatus, Fig. 149).

bisulphate[1] (*see also* Ger. Pat. 267,869, 1912, of the Saccharinfabrik vormals Fahlberg).

The condensing plant is, however, much more important than the distilling plant, and after many changes it has to-day reached a remarkable degree of perfection, so that all the gases which are evolved together with the HNO_3 vapours are obtained separately. These gases consist more especially of nitrogen trioxide (N_2O_3), HCl, nitrosyl chloride, chlorine, iodine (if the nitrate contains it), and probably also oxygen. The lower the temperature at which the sulphuric acid reacts with the nitrate the less nitrogen dioxide, NO_2, is formed. The HCl is formed by the action of the sulphuric acid on chlorides contained in the nitrate, and this HCl, in contact with nitric acid, is in turn partly transformed into chlorine and nitrosyl chloride, $NO_3H + 3HCl = NOCl + Cl_2 + 2H_2O$, and since HCl, Cl, and NOCl are evolved at lower temperatures, these are found in the first products of the distillation. If the nitrate contains perchlorates chlorine derivatives are also formed towards the end of the distillation. All these impurities are soluble in nitric acid, so that on simply condensing the vapours from the distillation, which was once the general practice and still is in certain works to-day, a very impure nitric acid is obtained, which must then be separately purified, whilst in modern plants pure nitric acid is obtained directly.

The old condensing systems were formed of two batteries of seven double-necked receivers which were superposed in series, with a final condensing tower for the vapours which escaped from them. The condensation was caused by the cooling effect of the external atmosphere in which the receivers were placed, and one can thus understand how the working was irregular at various seasons, because the difference in the outside temperature in winter and summer is often one of 40–50°. The numerous joints also favoured the escape of gas, and such plants occupied much space. The yield did not exceed 90 per cent. of the theoretical amount of HNO_3.

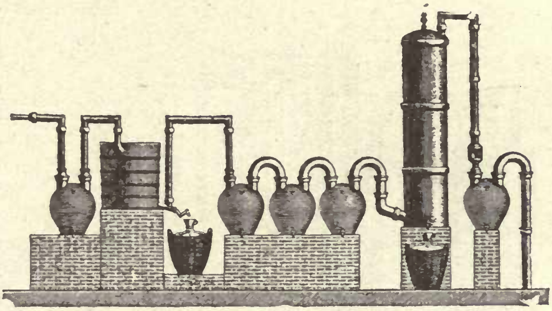


FIG. 148.

The first improvement which was introduced was the initial cooling of the vapours in a stoneware coil immersed in cold water, by which means the number of receivers was diminished.

These coils of baked stoneware, which are difficult to construct, were first manufactured in England. For the last fifteen years they have also been manufactured by Rohrmann in Kranschwitz, near Moscow, and by the earthenware works of Bettenhausen, near Cassel. Since the coils are costly they are preceded, in order to preserve them from damage, by a receiver (Fig. 148) which slightly cools the acid vapours and retains the solid and liquid

---

[1] The sodium bisulphate may then be utilised, by the Meyer-Oehler process (Ger. Pat. 136,998), for the manufacture of strong hydrochloric acid and sodium sulphate; the bisulphate is finely powdered and well mixed with a quantity of sodium chloride less than that required by the theoretical equation: $NaHSO_4 + NaCl = HCl + Na_2SO_4$. This mixture does not interact in the cold, but at 100° it reacts to the extent of 7 per cent., at 200° to 42 per cent., at 250° to 70 per cent., at 300° to 90 per cent., and at 400° to 98 per cent. It is heated in muffle-furnaces or cast-iron retorts, the internal temperature of which is 450°–500°. In this way a pure sulphate and a pure and very concentrated hydrochloric acid are obtained in the ordinary Cellarius receivers (*see* p. 176). One inconvenience of this process is the readiness with which the mixture of bisulphate and salt absorbs moisture and forms a paste in the feeding vessels. Uebel suggests the heating of the bisulphate in a retort to a temperature above the fusion point followed by pulverisation with compressed hot air (or chimney gases) from an injector, the mass being directed into a strongly-heated tower chamber; the solid particles which collect on the floor consist largely of normal sulphate and the decomposition is completed on the hot floor, the gaseous SO_3 and SO_2 being carried off (Ger. Pat. 226,110). L. Dior, on the other hand, suggests mixing the bisulphate with bauxite and a little wood charcoal and heating in a muffle furnace; the gases yield sulphuric and sulphurous acids, while in the furnace there remains sodium aluminate, which is used for the preparation of aluminium hydroxide (Belgian Pat. 227,686).

Hartmann and Benker (Ger. Pats. 204,353 and 204,703) utilise the bisulphate by fusing it with the normal sulphate and heating the mass in a furnace so as to cause evolution of concentrated sulphuric acid which is condensed in towers.

substances which are carried over. After passing through the coil the vapours which are not yet condensed pass through two or three receivers, and the last traces are retained in a plate-tower (Lunge-Rohrmann, *see* p. 299) with a water spray. The remaining gases, before passing up the chimney, deposit their moisture in a final receiver which is provided with a window in order that the colour of the gases passing out of the tower may be noted.

Acid thus prepared is of a strength of 36°, 42°, and 48° Bé., though the last acid which distils is always more dilute because the temperature is higher and the sodium bisulphate gives off water. It also contains a considerable quantity of nitrous fumes which colour the acid brownish yellow.

Guttmann and Rohrmann obtain nitric acid containing very little nitrous acid directly during the distillation by employing a series of seven long vertical condensing tubes of stoneware (Fig. 149) communicating with one another below by means of a single tube which collects the colourless condensed acid, whilst a current of hot air is blown into the delivery tube of the distillation apparatus (as is seen to the left of the figure) and carries the nitrous vapours which are not condensed through the final absorbing tower. The condensing tubes are immersed in a large vessel of water, the temperature of which may be regulated, and are preceded by a small receiver. By means of this apparatus a concentrated acid is obtained with a yield of 98 per cent. of that required by theory; in some works the condensation is now effected in simple glass tubes.

In 1891 Valentiner introduced with advantage the employment of a vacuum in the whole apparatus by means of a pump stationed at the end of the system. The vapours which are not condensed pass finally through several receivers containing lime in order that all the acid vapours may be absorbed and damage to the suction pump prevented. The lime must be frequently renewed.

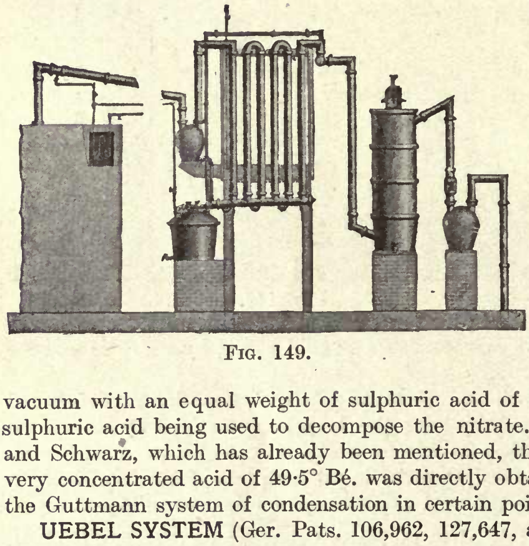


FIG. 149.

In the first plant for working with a vacuum sulphuric acid of 66° Bé. could not be employed to react with the nitrate because too much frothing occurred, and acid of 60° Bé. was used, a more dilute nitric acid of 40–43° Bé. being thus obtained. This acid had to be concentrated by distilling it in vacuum with an equal weight of sulphuric acid of 66° Bé., the remaining, more dilute sulphuric acid being used to decompose the nitrate. By a recent patent of Valentiner and Schwarz, which has already been mentioned, the process was much simplified and a very concentrated acid of 49·5° Bé. was directly obtained. In 1915 U. G. Paoli improved the Guttmann system of condensation in certain points.

UEBEL SYSTEM (Ger. Pats. 106,962, 127,647, and 170,532). Since 1900 the use of this process has been spreading in large chemical works, especially explosives factories, since it constitutes a continuous process and gives almost all the acid in a concentrated form, only 5–8 per cent. being dilute. Nitric acid of 95–96 per cent. strength can be obtained in 97–98 per cent. yield with a consumption of about 15–18 kilos of coal per 100 kilos of the monohydrate acid. To obtain continuous working, Uebel uses three horizontal vessels (1, 2, Figs. 150 and 151) heated by the same furnace—two large ones at the same level (1, Fig. 150) and a smaller one placed lower (2). Into one of the upper vessels, 1000 kilos of sodium nitrate are introduced by the orifice, *a*, about 1000 kilos of concentrated sulphuric acid being then added in one lot and the heating started with the hot gases which, during normal working, have already heated the lower vessel. After six hours, when the distillation of nitric acid is on the decline, the second upper vessel is charged with nitrate and acid, while the fluid mass of the first vessel is discharged, through a large tube, *c*, furnished with a slide, into the hotter lower vessel (2), in which the distillation is completed in 3–4 hours; the nitric acid from this vessel is, however, weaker and richer in nitrous acid, so that it is best condensed separately (6). At the tenth or twelfth hour the first upper vessel is recharged with fresh nitrate and sulphuric acid, while the bisulphate of the lower vessel is discharged at above 200° from the mouth, *d*, into suitable iron trucks in which it solidifies; the fluid mass of the second vessel is then at once discharged into the lower vessel to be heated with fresh nitrate. In this way each of the upper vessels receives two charges per 24 hours, but at different times, so that the evolution of nitric acid vapour is almost constant throughout. The earthenware condensation battery is also arranged on a rational basis: the nitric acid vapours from the two upper vessels unite in a small earthenware pot (3), from which they escape subdivided into two halves (4) to the bottom of two batteries (5). The earthenware pipes, 2 metres long and 12–15 cm. in diameter, are superposed almost horizontally and zigzag one into the other; they are cooled only by the surrounding air and the condensed acid descends slowly, owing

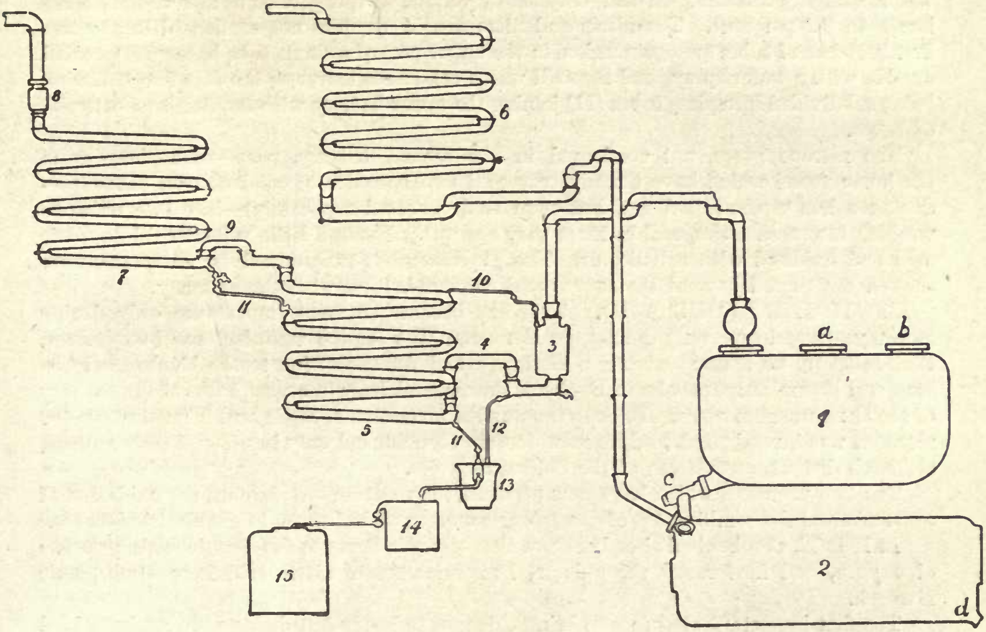


FIG. 150.

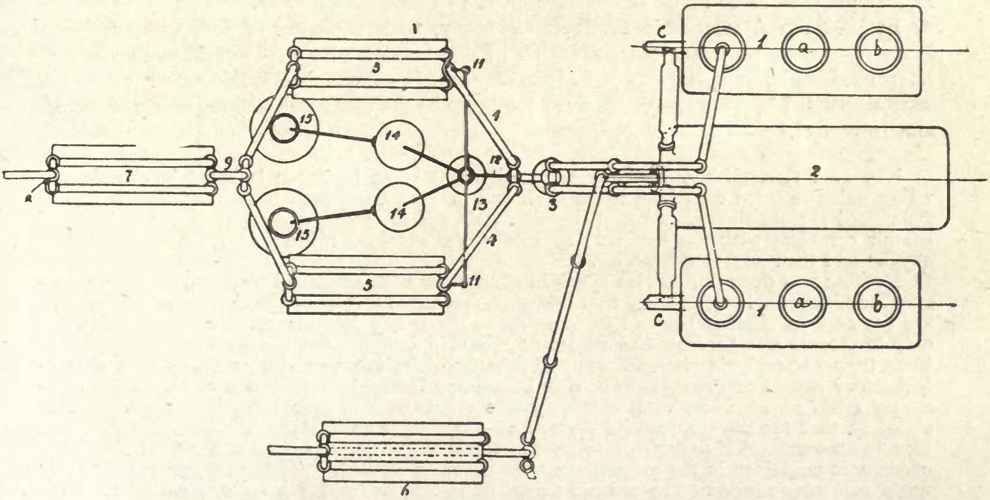


FIG. 151.

to the slight inclination of the tubes, and meets new hot gases and gives up to these its dissolved nitrous vapours. Thus, the condensed acid which collects in the earthenware jar (15), after passing through one or two earthenware coils (13 and 14) immersed in cold water, is highly concentrated and only feebly yellow, the proportion of nitrous acid being less than 0·2 per cent. The nitric and nitrous acid vapours not condensed in the two first batteries of tubes are again united in the upper part of a single tube battery (7), cooled outside with a water spray, and the acid which condenses traverses the first two batteries, being subdivided into glass tubes (11) joining the upper battery with the first two batteries of tubes.

The nitrous gases, not condensed in the second battery, pass—with those from the lower vessel which have already traversed two batteries of condensation tubes (producing a less concentrated and less pure acid collected separately)—into two or three washing towers in series, and in these they are washed with a little water or dilute nitric acid and oxidised with a little air. The gas current is maintained by an earthenware suction fan placed beyond the towers and communicating with the chimney.

SYNTHETIC NITRIC ACID. This has become of great importance only during recent years and especially during the European War for the manufacture of explosives, Chili saltpetre no longer arriving in Germany and Austria owing to the blockade of the seas, and becoming scarce also in England, France, and Italy in consequence of the activity of the German submarines. Prior to the war the formation of nitric acid from atmospheric nitrogen was investigated, and its manufacture then started only in view of the eventual, although distant, exhaustion of the Chilian deposits.

The two processes which have now attained the most importance are the oxidation of ammonia and the combination of atmospheric oxygen and nitrogen in the electric furnace.[1]

In 1892 W. Crookes had already shown that nitrogen burns in the electric arc in presence of oxygen, and he foresaw the industrial manufacture of nitric acid from atmospheric nitrogen.

The first important attempts to bring this new industry into being were made in 1896 by the electrotechnical firm of Siemens and Halske of Berlin (Ger. Pat. 85,103) by subjecting a mixture of 100 vols. of dry air and 1 vol. of dry ammonia to the dark electric discharge; solid ammonium nitrate was thus obtained and deposited on the walls of the containing vessel, but the process did not acquire any industrial importance.

The work of Nernst and the careful experiments of Muthmann, Hofer, and Lepel caused further progress to be made in the solution of this difficult problem.

In 1902 the Atmospheric Products Company, with a capital of £200,000, erected a fairly important plant for the utilisation of one portion of the power from the famous Niagara Falls, by applying a patent of Bradley and Lovejoy. In 1903, however, the works were suspended because the yields were too low and the plant was still too costly, delicate, and imperfect.[2]

---

[1] In 1781 Cavendish showed experimentally that when hydrogen is burnt in the air, the water which resulted contained nitric acid, and in 1786 he showed that when electric sparks are passed rapidly through a vessel containing air and an excess of oxygen all the nitrogen of the air combines with the oxygen. In 1798 Odier obtained nitric acid by strongly heating oxygen and then mixing it with air.

Nothing was done during this epoch in connection with combined nitrogen. It was necessary for Liebig (in 1840) to show that one of the principal factors of the fertility of the soil was the presence of nitrates before this question acquired any importance. It was, however, so easy to procure nitrates from the important Peruvian deposits that the synthetic production of them from atmospheric nitrogen was not thought of, and it was also necessary that electrotechnology should progress much further before any industrial application of Cavendish's discovery could be considered. It was only when, towards the year 1900, it was proved with certainty that the nitrate deposits were rapidly becoming exhausted, thus threatening a fatal blow to all our flourishing agriculture, that methods of utilising a portion of the 400 trillion tons of nitrogen contained in the atmosphere were seriously studied. Electrotechnology has to-day made enormous strides. The natural forces of waterfalls furnish a large quantity of cheap energy, and thus, after more than a century, the factors came together which caused attempts to be made to translate the forgotten experiments of Cavendish into practice. In these attempts nitrogen oxides and nitric acid were obtained by burning the nitrogen of the air at very high temperatures obtained by means of the hydrogen flame or by the electric discharge.

[2] The apparatus used at Niagara consisted of an iron cylinder 1½ metres high and 1·25 metres in diameter. A vertical steel shaft revolved in this and carried 23 superposed groups of six arms, each of which formed as many electrodes, with each of which again an electrode fixed on the internal wall of the cylinder corresponded. Thus 414,000 small electric arcs were made

Negative results were also obtained by the process of Kowalski, which was tried in 1904 in a large works.

It is necessary to bear in mind the temperatures of formation and decomposition of nitric oxide, because it is an endothermic product which is formed only at very high temperatures, but is also decomposed at high temperatures; in fact the equilibrium $N_2 + O_2 \rightleftarrows 2NO$, only gives 1 per cent. of NO at 2200°; 2 per cent. at 2570°; 3 per cent. at 2854°; and at 3327° 5 per cent. is not dissociated. It is only at temperatures below 1200° that NO no longer dissociates; for this reason Helbig at Rome in 1903 passed the electric discharge through liquid air at a temperature of — 190°, and obtained considerable quantities of unaltered nitrogen oxides (solid N_2O_3).[1]

The true industrial application was, however, started by Dr. Birkeland of Christiana, aided in his experiments by the young engineer, Eyde (1903). When the electric arc from an alternating current of high tension (5000 volts) is suitably influenced by strong magnets it assumes the form of a large disc which in suitable furnaces may acquire a diameter of 2 metres. This discovery of Birkeland was immediately applied practically, and after numerous experiments on an enormous scale a works commenced operations in May 1905 at Notodden in the Hitterer region of Norway, which produced daily by the Birkeland-Eyde process a quantity of nitrates corresponding with 1500 kilos of pure nitric acid. The mean yield during five months of continuous working was 550 to 600 kilos of pure nitric acid per kilowatt-year (the theoretical yield of the electric furnace should be 134 grms. of HNO_3 per kilowatt-hour, or about 950 kilos per kilowatt-year). There is every promise of an increase in the yield and of the introduction of further improvements in the process, since a good part of the energy employed is still lost in the formation of heat, of which 30 per cent. is used for the concentration of the calcium nitrate solutions, 40 per cent. for heating the steam boilers, and 10 per cent. for pre-heating the air which enters the furnaces, while 17 per cent. is lost through radiation. Both horizontal and vertical furnaces were tried (*see* Fig. 152). It has now been shown that the horizontal furnaces are the better. The electrodes are made of copper and are hollow so that they may be kept cold by means of a current of water, thus avoiding the expensive breakages which easily occur with ordinary electrodes.

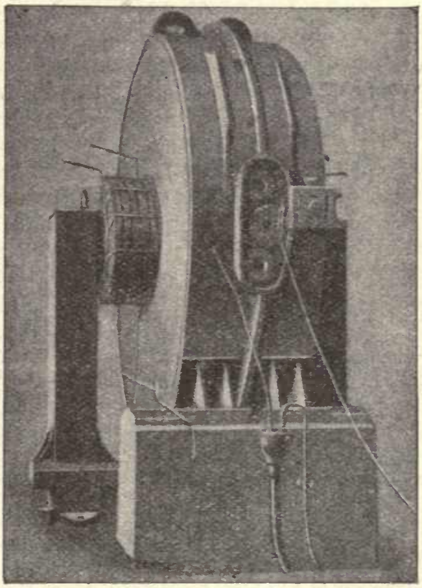


FIG. 152.

The gases which pass out from these electric furnaces are very hot and contain 1 to 1½ per cent. of nitric oxide (NO). In order that the oxide may not be decomposed it is necessary to cool the gas rapidly, and these gases are therefore used to heat the steam boilers and to concentrate the nitrate solutions, which are produced in the works. During

---

and broken every minute. This delicate and costly apparatus, however, gave a very small yield, not exceeding 430 kilos of nitric acid per kilowatt-year; it gave also a certain amount of nitrous acid, so that the nitrates obtained were too rich in nitrites.

[1] The molecular concentrations (C) in the chemical equilibrium resulting from the reaction: $N_2 + O_2 \rightleftarrows 2NO$, are represented by the ordinary equations (p. 372): $K = \frac{C_{(NO)^2}}{C_{(N_2)} \times C_{(O_2)}}$. The constant K is defined for every temperature (p. 392) by the formula, $\frac{d \log K}{dt} = \frac{Q}{RT^2}$ (*see* p. 379), in which R is the gas constant, Q the heat of reaction, and T the absolute temperature of the system. With given concentrations of oxygen and nitrogen there corresponds a definite concentration of NO. The heat of reaction, Q (*i. e.*, the heat produced when 1 gram-mol. of nitrogen reacts at temperature T with 1 gram-mol. of oxygen to give 2 gram-mols. of nitric oxide), is in this case negative, there being absorption of heat (2 × 21,500 cals.) in the reaction, so that the value of K (and also the concentration of NO) increases with rise of temperature.

this phase the nitric oxide below 600° and in contact with excess of atmospheric oxygen is transformed into the dioxide NO_2, and the current of gas then passes through granite towers from the top of which a spray of water falls and transforms the nitrogen dioxide partly into soluble nitric acid and partly into nitric oxide; the latter in turn combines with the oxygen of the air forming dioxide, which is then absorbed in other towers and so on.[1] The dilute aqueous solution of nitric acid is repeatedly pumped to the top of the towers until nitric acid of 50% concentration is obtained, and is then transformed by means of lime and marble into calcium nitrate and evaporated.

Ordinary calcium nitrate is not suitable for agricultural purposes because it is deliquescent, but it has been found that *basic calcium nitrate* remains dry and may be converted into a powder suitable for spreading over the ground. In soils which are somewhat acid through the presence of carbon dioxide it forms calcium carbonate and normal calcium nitrate which is deliquescent, thus soon reaching the roots of the plants. The calcium nitrate so prepared always contains a little calcium nitrite, which is by some considered harmful to germination, whilst, on the other hand, it appears not to be harmful if distributed over the seed when this is already somewhat developed.

Calcium nitrate has the advantage over Chili saltpetre that it does not contain perchlorates, that sodium salts do not accumulate to any extent in the soil, and that it has a beneficial effect on soils which show a deficiency of lime. Further, it is assimilated by plants better than sodium nitrate.

Calcium nitrate containing 13 per cent. of nitrogen now costs £4 8*s.* per ton, whilst sodium nitrate containing 15·5 per cent. of nitrogen costs from £8 16*s.* to £10 8*s.* per ton.

In 1905 the Franco-Norwegian Company was formed at Christiania with a capital of £280,000, to utilise a waterfall of 40,000 h.p. in Telemarken, Norway, for the manufacture, by the Birkeland-Eyde process, of *nitric acid* and *alkali nitrates* and *nitrites.* The latter can be obtained in abundance if the gas from the electric furnaces is absorbed by much cold water, and if the gases, before absorption, are mixed at 250° with steam.

[1] The reaction, $2NO + O_2 = 2NO_2$, is exothermic, so that to obtain more NO_2 it is necessary to cool the system, but NO being an endothermic compound, would tend to dissociate when cooled and to diminish the yield of NO_2. Whereas, however, the velocity of dissociation of NO into N_2 and O_2 is very high at 3000°, it becomes millions of times less below 1000°; hence, if the gases are cooled rapidly as soon as they leave the electric furnace, the dissociation is reduced to a minimum.

As is well known, the velocity of reaction or of dissociation is doubled for every 10° rise of temperature, so that a rise of 1000° would increase the velocity 10^{33} times; a drop in temperature from 3100° in the electric furnace to 900° would diminish the velocity $3 \times 3 \times 10^{12}$ times. Nernst (1906) calculated that the velocity of the reaction, $N_2 + O_2 = 2NO$, at 1500° abs. is such that one-half of the theoretical equilibrium concentration (0·10 per cent. NO) is reached in 30 hours, whilst at 2900 abs. one-half of the theoretical concentration (3·20 per cent.) is reached in 100 hours. The inverse reaction, $2NO = N_2 + O_2$, requires the following times to reach one-half of the theoretical dissociation at various temperatures:

At	900°	abs.	$7{\cdot}35 \times 10^3$	minutes.
,,	1500°	,,	3·30	,,
	2100°	,,	$1{\cdot}21 \times 10^{-3}$	,,
,,	3100°	,,	$2{\cdot}25 \times 10^{-9}$	,,

It is evident that, if the gases leaving the electric furnace are not quickly cooled, the dissociation of the NO is extraordinarily rapid, dissociation to the extent of one-half occurring in little more than three minutes at 1227° (1500° abs.), whilst about 2200 minutes (almost 37 hours) are required at 627° (900° abs.).

The degrees of dissociation of $2NO_2$ into O_2 and 2NO are (Richardson, 1887):

At	130°	and	718·5	mm.	pressure,	0 %.
,,	184°	,,	724·6	,,	,,	50 %.
,,	620°	,,	760	,,	,,	100 %.

Briner and Durand (1913) have studied the conditions in which HNO_3 and HNO_2 are preferably formed on absorption of the nitrous gases by water. The three following reversible reactions characterise the different states of equilibrium: (1) $N_2O_3 + H_2O \rightleftarrows 2HNO_2$, (2) $2NO_2 + H_2O \rightleftarrows HNO_2 + HNO_3$ and (3) $3HNO_2 \rightleftarrows 2NO + H_2O + HNO_3$. The liquid phase always contains all these components. If N_2O_3 is treated with excess of water (1), reaction (3) is also favoured and there remain only traces of N_2O_3 in solution (these, however, impart a slight blue colour to the solution). Since reaction (3) is endothermic (— 18·3 cals.), rise in temperature will help the decomposition of HNO_2 and the formation of HNO_3; indeed, the molecular ratio $\frac{HNO_2}{HNO_3}$ is found experimentally to be 1·54 at 0°, 1·32 at 17°, 1·02 at 30°, and 0·76 at 40°. Increase of pressure and lowering of the temperature, on the other hand, favour the formation of HNO_2.

At Notodden in 1909 36 electric furnaces were working. These are constructed of cast steel and of wrought-iron, lined with refractory bricks in such a manner that a chamber of circular section is formed into which the electrodes are introduced (Fig. 153). The first furnaces were of 500 h.p., but later 4000 kilowatt furnaces were employed.

The electrodes have to be changed every three or four weeks and the fireproof lining of the furnace every four or six months. The temperature of the flame of the arc is about 3500°. The products of reaction escape from the furnace at a temperature of 800° to 1000°, and they pass through two conduits of 2 metres diameter to four boilers, where their high temperature is utilised for the production of steam to be used to concentrate the liquids obtained later.

The gases then pass through a large number of *aluminium tubes* (cooled by a current of water) into cylinders of wrought-iron lined with acid-proof bricks, where the oxidation of the nitric acid is completed. They then pass to the absorption towers.

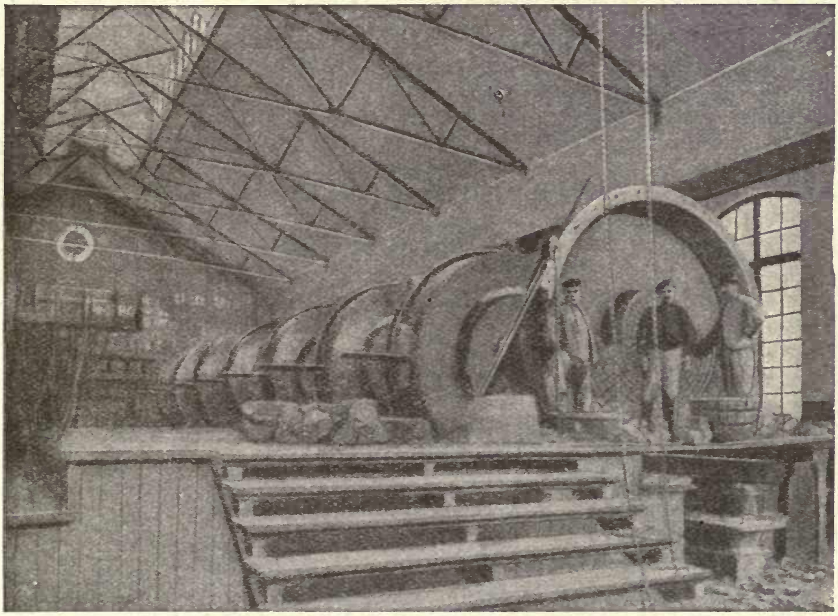


FIG. 153.

The towers of the first series (filled with quartz) are of granite and are fed with water, whilst those of the second series (filled with pieces of quartz) are of wood and are fed with soda solution. The gas passes from the furnaces to the towers through the action of an aluminium fan; the absorbing liquid circulates in the granite towers until it finally contains 35 per cent. of nitric acid by volume, and is then run into granite cisterns and finally into granite channels containing limestone. The solution of calcium nitrate thus obtained is concentrated *in vacuo* and then poured into iron drums or into shallow iron pans; the solution of sodium nitrate which is formed in the wooden towers is concentrated in a similar manner and allowed to crystallise.

In 1909 about 40,000 h.p. were used at Notodden and 12,000 tons of calcium nitrate were produced (sold under the mark "Norge"),[1] besides 2700 tons of sodium nitrate

---

[1] A sample of commercial "Norge" in brownish powder with small lumps, with a nitrogen content of 12·6 per cent., gave the following results on analysis :

Calcium nitrate, $Ca(NO_3)_2$	74·15 %
Calcium hydroxide, $Ca(OH)_2$	9·80 %
Moisture	15·88 %
Insoluble matter	1·53 %

Another sample gave : moisture, 20·17 %. *Soluble in water :* nitrogen as nitrate, 13·32 %; nitrous acid, 0·03 %; total lime (CaO), 26·98 % (0·04 % as free hydroxide); magnesia, iron and 370 tons of mixed sodium nitrate and nitrite, the production in 1908 being one-fourth less. In 1911, 25,000 tons of calcium nitrate and 400 tons of sodium nitrite were made, and in 1915, 70,000 tons of calcium nitrate.

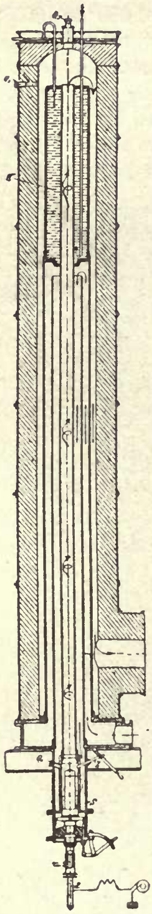


FIG. 154.

The Birkeland process is already able to compete with Chili saltpetre, since the hydraulic power utilised in Norway enables an electric h.p.-year to be obtained at a price of only 12*s*. It would not, therefore, be applicable in any other country with the yields at present obtained, owing to the considerably greater cost of electrical energy.

With such yield all the waterfalls in Europe would not suffice for the complete replacement of Chili saltpetre by artificial calcium nitrate, and, however much the Birkeland process may be improved by itself, it would with difficulty suffice to satisfy the needs of agriculture. Better yields in the electric furnace may be obtained, either by vigorously cooling the zone of the furnace surrounding the arc (in this way Haber attained a concentration of 8·3 per cent. of NO), or by working at reduced pressures, or by raising the temperature of the zone of the arc, or by increasing the proportion of oxygen in the air,[1] or, best, by subjecting only the oxygen to the action of the electric discharge to dissociate it into active atoms, which, as was shown by Fischer (*see* chapter on Oxides of Nitrogen), then combine at once with the nitrogen. A proposal has been made to treat phosphorites directly with the dilute nitric acid first obtained and thus avoid the expense of concentration. In this way a superphosphate containing a large percentage of nitrates would be obtained (diphosphate, *see* Bretteville patents and Ger. Pat. 217,309).

Meanwhile, however, the bold initiative caused further progress, and new processes arose which allow one to foresee a great development of this marvellous industry of the combustion of atmospheric nitrogen in the near future. Haber and König found that on using rarefied air and an excess of oxygen the action of the electric arc leads to a concentration of 14 per cent. of nitric oxide, but it does not appear easy to apply this process practically on an industrial scale. A large works is, however, already under construction at Christiansand in southern Norway to apply the new electrical process of the Badische Anilin und Soda-fabrik of Ludwigshafen, patented in 1905 (Ger. Pats. 201,279, 204,997, and 212,051); these patents are based on the work carried out by Brunck since 1890 and completed in the works at Ludwigshafen by Schönherr and Hessberger, who obtained industrial yields equal, and perhaps superior, to those of Birkeland and Eyde. In a long vertical iron tube open above, which acts as an electrode, an electric arc is made to pass by approaching another insulated electrode to within a few millimetres of the base. If a current of air is now passed tangentially into the lower part of the tube (Fig. 154) in such a manner that a spiral motion is produced, the flame of the arc increases in length, following the air current, and finally fills the whole of the tube and becomes strongly luminous, especially along the axis (Fig. 155); at the top of the tube a collecting tube carries off the

---

and alumina, traces. *Insoluble in water*, 1·325 %: calcium carbonate, 0·444 %; magnesia (MgO), 0·249 %; iron and alumina ($Fe_2O_3 + Al_2O_3$), 0·348 %; manganese (Mn_3O_4), 0·019 %; soluble silica (SiO_2), 0·163 %; insoluble silica (sand), 0·103 %.

The moisture is difficult to determine in an oven at 105°, since it requires as long as three weeks under these conditions, whereas when 4–5 grams of the substance are heated in a platinum crucible with a very small flame distant 10 cm. from the base of the crucible, the semi-fused mass becomes constant in weight after twenty minutes.

[1] Application to the reaction, $N_2 + O_2 = 2NO$, of the equation of equilibrium, $K = \frac{(NO)^2}{(N_2)(O_2)}$, shows that increase in the oxygen produces increase in the NO; if equal volumes of nitrogen and oxygen are used, the amount of NO should theoretically be increased by 25 per cent. in comparison with that resulting from the use of atmospheric air. In certain experimental furnaces the increase is as high as 30 per cent., possibly owing to partial dissociation of the oxygen and nitrogen molecules; for the reaction, $N + O = NO$, the theoretical increase is 51 per cent. (*see* chapter on Oxides of Nitrogen).

air, which contains up to 2 per cent. of nitric oxide. The tube may also be constructed of non-conducting material, and then the continuous arc is started by placing a metallic spiral inside it.

Nitric oxide is formed in the arc, especially along the axis, and is gradually repelled from the centre to the circumference, where the colder air prevents its decomposition; the upper part of the tube is cooled outside by means of water.

A small industrial trial plant with these tube-furnaces was constructed at Christiansand in 1907 with furnaces of 600 h.p. and also of 1000 h.p. and an alternating current at 4200 volts. Long luminous arcs up to 7 metres in length were obtained with an air current of 1100 cu. metres per hour. The air entered below through adjustable openings by means of which the length of the arcs could be controlled (Fig. 156). The lower electrode is hollow and made of iron and can be cooled internally with a current of water. The hot gases which escape from the furnaces pass into an annular tube in the interior of which a current of cold air passes in the opposite direction and is thus preheated before passing into the furnace, whilst the hot gases are cooled by it. The nitric oxide mixed with air, when cooled below 600°, commences to react with the oxygen, being slowly transformed into the dioxide (NO_2), the gaseous mass then assuming a brown colour. The nitrogen dioxide is in turn transformed in contact with cold water into nitric acid to the extent of two-thirds, whilst the other third regenerates nitric oxide according to the following equation:

FIG. 155.

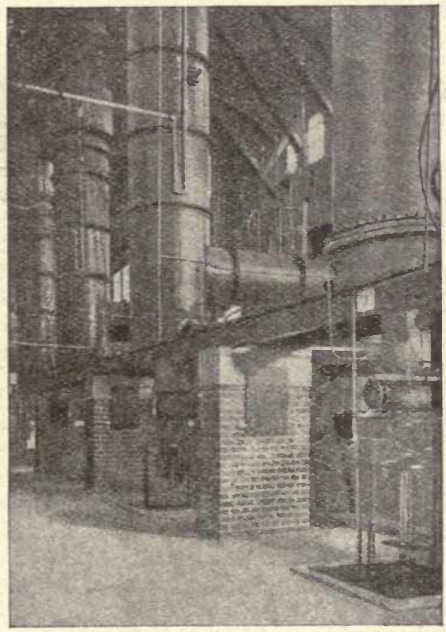


FIG. 156.

$$3NO_2 + H_2O = 2NO_3H + NO;$$

the latter is again transformed into dioxide by the excess of air and so on. By repeatedly utilising the same water a solution of nitric acid of 40 per cent. strength is obtained.

In the Schönherr furnace and probably also in other furnaces, only 3 per cent. of the electrical energy is utilised as chemical energy to form NO; 40 per cent. is recovered from the water used to cool the gas and 30 per cent. from the hot gases which heat the steam boilers, while 17 per cent. is lost by radiation and 10 per cent. in the water which cools the electrodes.[1] It is said that the Schönherr furnaces were abandoned in 1914.

[1] A great dissipation of energy undoubtedly accompanies the manufacture of nitric acid starting with the synthesis of nitric oxide, this being more endothermic than syntheses of the higher oxides of nitrogen (*see* chapter on Oxygen Compounds of Nitrogen). Theoretically the most advantageous would be the direct synthesis of nitric acid from its elements ($H_2 + N_2 + 3O_2 = 2HNO_3 + 2 \times 35{,}000$ cals.), which is strongly exothermic; if steam were used, it would also be exothermic ($2N_2 + 5O_2 + 2H_2O = 4HNO_3 + 4 \times 15{,}000$ cals.), but up to the present the problem has not been found soluble in this sense on a practical scale.

The transformation of the NO into NO_2 occurs in large lead chambers, and the nitric acid is formed in granite towers filled with lumps of quartz in order to subdivide and mix intimately the water which falls from above and the gas which enters below; the gases which escape from the first towers are washed with milk of lime in other towers.

The solution of nitric acid is then treated with lime and concentrated *in vacuo* in multiple effect evaporators; it is finally heated in furnaces, basic calcium nitrate containing 13 per cent. of nitrogen being thus obtained.

In 1909 Schlösing proposed to avoid the intermediate preparation of nitric acid by passing the gases, while still hot (350°) and containing nitrogen dioxide, directly over solid slaked lime arranged in the form of bricks inside iron tubes. In this way calcium nitrate is at once obtained together with free lime and a little calcium nitrite.

Almost pure sodium nitrite or calcium nitrite may also be obtained from nitrogen dioxide if it is treated with hot caustic soda solution or milk of lime in granite towers, although theoretically it should be more advantageous to work in the cold (*see* Note, p. 392); in the first case the nitrite is perhaps formed with loss of NO_2 : $4NO + 2NaOH = 2NaNO_2 + N_2O + H_2O$, whilst with milk of lime in the cold the NO of the N_2O_3 (*i. e.*, $NO_2 + NO$) is also converted into nitrite.

In 1907 the Franco-Norwegian Company of Notodden combined with an industrial group, headed by the Badische Anilin und Soda-Fabrik, and this combination formed two distinct companies; one, with a capital of £880,000, was founded for the utilisation of the large hydraulic powers of Norway and the transformation of these into electrical energy; and the other, with a capital of £1,000,000, was formed for the erection of works to manufacture calcium nitrate, nitrite, and synthetic nitric acid. Works for obtaining 140,000 h.p. from 10 turbines of 14,000 h.p. each are already well advanced. This power is all to be obtained from a single fall of 50 cu. metres of water and a further 100,000 h.p. are to be produced from a second fall at Telemarken-Rjukan.

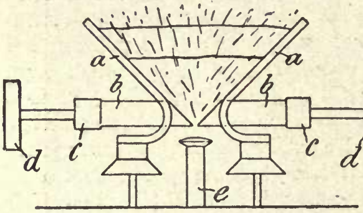


FIG. 157.

About 1912 the Badische Anilin und Soda-Fabrik withdrew from the industry in Norway, and later they induced Eyde to abandon his position as technical director and, with capital mainly Norwegian and French, formed the "Société Norvegienne de l'azote et des forces hydroelectriques" (which in 1913 increased its capital from £2,240,000 to £3,800,000) for the manufacture of calcium nitrate ("Norge"), sodium nitrate, ammonium nitrate, sodium nitrite and nitric acid, and for the production of hydro-electric energy. In the Rjukan works alone 250,000 h.p. are utilised, and in 1914 further factories were started to make use of 150,000 h.p. at the falls of Tyin and Matle, so that in a few years' time the amount of nitrogen used in Norway will correspond with 250,000 tons of calcium nitrate per annum. In 1912 this company paid a dividend of 8 per cent. on the preference shares and 6 per cent. on the original shares. In the first half of 1913, the company exported from Norway 32,956 tons of "Norge" nitrate (only 15,758 tons in the corresponding period of 1912), 11,000 tons of calcium cyanamide (6,740 tons in 1912), 4,246 tons of ammonium nitrate, and 2,764 tons of sodium nitrite.

We may thus readily comprehend how much hydraulic energy will be necessary one day in order to replace all the nitrate now supplied from Chili, namely, 1,800,000 tons, and it is evident that this day is still a long way off, so that a rapid change in the commercial prospects of natural nitrate is not to be feared.

Simultaneously with the large works in Norway a large works was erected at Patsch near Innsbruck (Tyrol), where the electric arc was diverted by the process of the Brothers Pauling (Ger. Pats. 193,366, 198,241, 205,018, 213,710, 244,840, 246,712, and 257,809) by blowing in air between two electrodes impinging at angle (Fig. 157). In this way a fan-shaped flame about 1 metre long was obtained (Fig. 158). At Patsch there are 24 very simple electric furnaces utilising 15,000 h.p., and up till now the gases which are obtained contain 1½ per cent. of nitric oxide with a yield of about 500 kilos of nitric acid per kilowatt-year. Sodium nitrite and nitric acid of a concentration of about 35 per cent. are manufactured. Attempts to concentrate this acid by electrolytic means (Ger. Pat. 180,052) have not yielded practical results, and concentration by means of sodium bisulphate does not appear very convenient. Although the unit of nitrogen in nitric acid is worth three times as much as in calcium nitrate, the economical concentration and the sale and transport of this acid do not constitute an easy problem. In 1913 a new Pauling plant was started in America to utilise the falls of the Cataroba river (Great Falls). The first works erected on the Pauling system in Italy (at Legnano) by the Rossi Electro-chemical Company were designed to utilise 10,000 electrical h.p. (eighteen 450 kilowatt furnaces with current of 50 alternations) during the ten night hours when the power was not required by other industries. The power thus obtained costs less than £1 per kilowatt-year, but is available for only ten hours per day. In 1915 Rossi erected another works at Ponte Mammolo (Rome). Another Pauling plant has been started in France (at La Roche de Rame) with 20,000 h.p. in nine furnaces.

Attempts made in 1907 and 1908 by the Electro-Chemical Company of Caffaro at Brescia, utilising patents of Dr. Helbig of Rome, could also not be applied industrially on a large scale because the yields were still too low, and more especially because the cost of electric power in the vicinity was too high. Better results were obtained by Helbig at Gampel (Switzerland) with a 300-kilowatt furnace.

Helbig's furnace is very simple and is easy to work and regulate (U.S. Pat. 926,413). It contains three electrodes and is worked with a three-phase high-tension current. The flame of the arc is widened to a disc by means of a stream of compressed air which is passed between the electrodes from two capillary tubes placed in front of, and perpendicular to them.

An attempt has also been made to increase the yield of oxides of nitrogen in the electric furnace by the injection of hydrocarbons (Ger. Pat. 209,966). Further, it has been shown that, when carbon monoxide is burnt in presence of air under pressure in a closed vessel and the flame cooled immediately against cold walls, oxides of nitrogen and therefore nitric acid are formed (French Pat. 396,375, 1908).

None of the processes yet applied to the utilisation of atmospheric nitrogen is capable of competing permanently with Chili saltpetre as a chemical fertiliser, such processes serving rather to give a supplementary production to supply the ever-growing agricultural and industrial demands. The consumption of energy in the fixation of one kilo of nitrogen by the various processes is as follows: Pauling, 71; Birkeland-Eyde, 62; Schönherr, 59; calcium cyanamide, 24; and Serpeck, 12 kilowatt-hours.

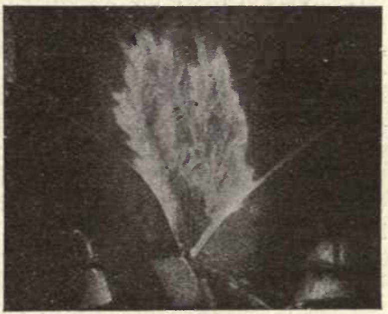


FIG. 158.

In any case it is necessary to remember that it is not possible to manufacture nitrate from atmospheric nitrogen profitably without the use of a large source of hydraulic power costing not more than £1 4*s.*–£1 12*s.* per h.p.-year in the form of electrical energy, and unless it is possible to give the holders of the patents an interest in the concern, instead of paying them the usual fabulous sums in advance, because in industries of this kind improvements and modifications are possible from one day to another, and a new patent may cause the value and advantage of those preceding it to be lost. In order to avoid unfortunate disappointments, extreme caution is also necessary, as these new processes are very attractive, but just as rich in financial surprises if they are involved from the beginning in excessive liabilities for patents, etc. In normal times concentrated nitric acid, as required for making explosives, colouring matters and different chemical products, is best manufactured from Chili saltpetre, whilst for the production of the dilute nitric acid required by sulphuric acid works to replace nitre for the lead chambers or used for preparing ammonium nitrate, etc., synthetic methods may be used.

From synthetic calcium nitrate it may, perhaps, be possible one day to obtain concentrated nitric acid. According to Ger. Pat. 208,143, dry calcium nitrate is treated with concentrated sulphuric acid, the reaction being started by addition of a little nitric acid; the reaction then proceeds in the cold and yields concentrated nitric acid and insoluble calcium sulphate, which is afterwards separated by filtration. Traine and Hellmers (Ger Pat. 269,656, 1912) mix the reacting mass with a large proportion of powdered quicklime no incrustations being then formed on the walls of the retort.

SYNTHETIC NITRIC ACID FROM THE OXIDATION OF AMMONIA. The preparation of nitric acid by oxidation of ammonia has assumed industrial importance only during the last few years and more especially during the European War, owing to the difficulties attending the importation of nitrate from Chili. The reaction was studied as long ago as 1839 by Kuhlmann, who oxidised the ammonia by atmospheric oxygen in presence either of spongy platinum heated at 300° or of finely divided nickel or copper as catalyst. Kayser mixed with the ammonia air previously rendered more active by means of the dark discharge and used as catalyst thin sheets of platinum or palladium, which gave a yield of 70 per cent. Only after 1900 was a rational physico-chemical investigation of this reaction undertaken by Ostwald and Brauer, who attempted to develop from it a practical process (French Pat. 317,544; Swiss Pat. 25,881; Eng. Pat. 698, Jan. 9, 1903, and Austrian Pat. 37,136); the German patent was not granted owing to the earlier work of Kuhlmann, Kayser, Warren (1891), Marston (1901), etc. As catalyst Ostwald mentions various substances,[1] but the best results are obtained with thin sheets of platinum, covered or not with platinum sponge and arranged, wavy and inclined, on various horizontal planes so as to be completely surrounded by the air-ammonia current meeting them at a certain definite velocity, the catalyst being maintained at dull redness just visible in the daylight. The apparatus is of nickel steel (Ger. Pat. 207,254) or aluminium (Swiss Pat. 41,262) in all parts where there is no condensation of nitric acid; then come pipes of earthenware or lead; the industrial yields appear to have exceeded 90 per cent. If the gases meet the catalyst with a low velocity the yield is practically zero. The formation of nitric acid is due to an intermediate reaction, the final reaction leading to nitrogen and water.

According to the conditions, the oxidation of ammonia may take place in different ways, more especially as follows: (1) $NH_3 + 2O_2 = HNO_3 + H_2O$; (2) $4NH_3 + 7O_2 = 4NO_2 + 6H_2O$; (3) $4NH_3 + 5O_2 = 4NO + 6H_2O$.

Reactions (1) and (2) occur with diminution of volume and are hence facilitated by working under pressure, whereas (3) is accompanied by increase in the volume and is hence favoured by reduced pressure.

Reaction (1) is markedly exothermic and the best yields are consequently obtained by keeping the temperature low, but not so low that the velocity of the reaction becomes less than is convenient in practice; for this reason catalysts are chosen[1] which accelerate the reaction even at comparatively low temperatures.

Below 140°, however, the reaction is too slow even with catalysts, while above 600° the yield should theoretically be lowered somewhat. In practice, however, a temperature of 700° is found convenient, on condition that the gases impinge on the catalyst with a considerable velocity; otherwise the products of the reaction are dissociated and free nitrogen formed, with marked diminution in the yield. The maintenance of the catalytic mass at 700° requires 10 kilowatt-hours per 100 kilos of nitric acid produced. With 47 grms. of catalyst, 100 kilos of HNO_3 can be produced per day with a loss of 3 per cent. of the platinum per month, but the catalyst must be renewed once a month as it becomes inactive.

In Germany use is made as catalyst of thorium oxide or tellurium oxide, sometimes mixed with rare earths (cerium oxide), as suggested by Frank and Caro. Morton suggests plumbates of Mg, Zn, Al, or Cd at 750°, while Bayer patented the use of ferric oxide, cuprous oxide, etc., especially to obtain nitrous acid at 600–700° from a current of air containing 4–5 per cent. ammonia by volume (Ger. Pat. 168,272, 1904).[2]

As regards mass action in these chemical equilibria, it is noticed that, if the ammonia is in excess ammonium nitrate also is formed in the reaction, whilst with the theoretical proportion of equation (1) an almost theoretical yield is obtained under certain conditions. Nevertheless, according to some patents the proportions of NH_3 and O_2 should be as indicated in equation (2). while Matignon (1916) is of opinion that the reaction must be

---

[1] Palladium, platinum, rhodium, iridium, and the following oxides (as well as the corresponding metals): MnO_2, PbO_2, Ni_2O_3, Co_2O_3, Fe_2O_3, Ag_2O, and CuO.

[2] Various patents have been taken out for the electrolytic oxidation of ammonia, but the industrial results are not encouraging. For instance, ammonium carbonate is transformed to the extent of 96 per cent. into ammonium nitrate at a platinum anode, but while the yield rises with the current density, it diminishes with increase in the nitrate, which undergoes reduction (with corrosion of the platinum anode); this may, however, be avoided by addition of ammonium bichromate.

expressed by equation (3), since NO_2 [equation (2)] cannot exist undissociated at the temperature employed.

In any case it is indispensable to use gases (NH_3 and air) which have been purified—more especially from dust—and freed from poisons such as hydrogen phosphide, acetylene (in ammonia from calcium cyanamide), siliceous powders, and volatile derivatives of silicon.

The industrial plant used in Germany for the oxidation of ammonia appears to be based on the type shown diagrammatically in Fig. 159, batteries of a number (up to 30) of small units each with 50 grms. of platinum being employed. Thirty such units give 200 kilos of 30 per cent. acid per twenty-four hours with a loss of 1·5 grms. of platinum.

The platinum catalyst is distributed in the chamber 4 and the electric current enters at 5; the water for regulating the temperature of the gas enters at 6 and escapes at 7; the air and ammonia arrive at 1 and 2 respectively and the temperature in the catalytic chamber is observed by means of a window, 8; samples of gas for analysis are drawn from 9 and the gases pass to the leaden condensation chamber through an aluminium tube, 10.

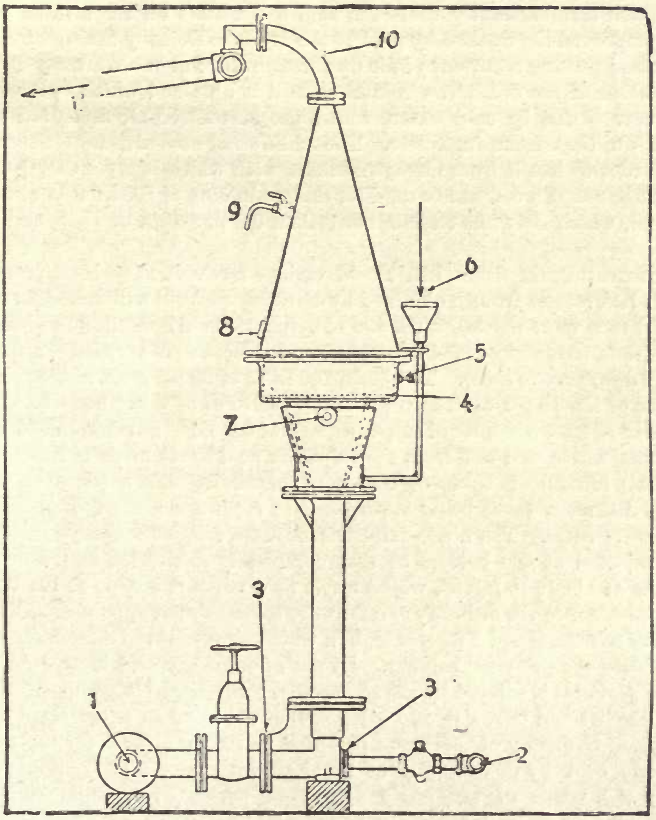


FIG. 159.

The Ostwald patents for England were acquired in 1910 by the Nitrogen Products and Carbide Company (London), which has a capital of £2,000,000 and proposes to utilise 400,000 h.p. in Iceland and 600.000 h.p. in Norway to manufacture calcium carbide, calcium cyanamide and, partly, ammonia to transform into nitric acid by the Ostwald process. The first important plant was erected at Vilvorde (Belgium) to produce nitric acid of 40-45 per cent. concentration, which was then concentrated by means of sulphuric acid. On the invasion of Belgium during the European War, this works was utilised by the Germans.

In 1909 a works to produce nitric acid by the Ostwald process was erected at Gerthe

(Westphalia) with a capacity of 2,400 tons of 53 per cent. nitric acid (with a yield of 90 per cent. on the ammonia used) per annum, and in 1912 it produced 130 tons monthly of ammonium nitrate, starting from purified ammonia from coal, although synthetic ammonia was at first thought to be indispensable for this process.

A large part of the nitric acid made in Germany during the European War was prepared by the Ostwald process and some of it by Frank and Caro's catalytic modification.

In 1916–1917 a large plant was erected in the explosives factory at Angoulême (France), which at the beginning of 1917 produced daily 30 tons of nitric acid, the ammonia being derived from calcium cyanamide.

In order to decolorise and refine the acid, which is brownish-yellow owing to the presence of nitrous acid, it suffices to heat it to a temperature of 60–80°, and to pass a current of dry air through it. The operation is shortened by the direct employment of a current of hot air which simultaneously heats the acid and carries off the nitrous vapours. In 1888 Hirsch improved the method by passing the crude acid slowly through a coil immersed in hot water and passing a current of air up through the coil in a contrary direction. By careful regulation of the outflow, a colourless acid is obtained which is then cooled in a second coil surrounded by cold water, whilst the current of air saturated with nitrous fumes passes into the condensing tower. The addition of urea nitrate to the acid has been proposed in order to free it from nitrogen oxides, with which it gives $CO_2 + N + H_2O$.

In this manner such a coil can be used for the production of 100 kilos per hour of colourless nitric acid, which does not contain more than 0·3 per cent. of N_2O_3 and is free from chlorides.[1]

For concentrating the dilute nitric acid various methods have been proposed of late years, but the best results are still obtained by distilling the acid with sufficient concentrated sulphuric acid to give at the end a residue of sulphuric acid containing at least 65–70 per cent. H_2SO_4 (thus 100 kilos of 93–94 per cent. or 66° Bé. sulphuric acid can fix 22–25 kilos of water from dilute nitric acid). To obtain 100 kilos of 90 per cent. nitric acid (47·5° Bé.) from 200 kilos of the 45 per cent. acid (32° Bé.), 100 kilos of water must be withdrawn by distillation with at least 600 kilos of sulphuric acid of 60° Bé. Further, in order to separate the concentrated nitric acid well from the sulphuric acid use is made of rectifying columns (as for alcohol) formed of tubes of cast-iron containing silicon (tantiron or helianite) 30–40 cm. in diameter, these being superposed to form a column 6–7 metres high filled with earthenware rings. The nitric-sulphuric mixture falls as a spray, while a small jet of steam is injected at the bottom so that completely denitrated sulphuric acid is discharged below at about 100–105°, whilst nitric acid vapours escape at the top at 70–80° and, before passing into the ordinary earthenware condensation apparatus, traverse a small dephlegmating column about 2 metres high in which a little of the dilute acid is condensed to flow back into the principal column. Excess of sulphuric acid is used for the concentration, since part of it is diluted by the steam used for heating [Pauling; Rossi (Legnano); French Pat. 455,531 and Ger. Pat. 236,341 (1909) of the Swedish Nitric Syndicate].

The Elektron Company of Griesheim patented in 1905 a process for the concentration of dilute nitric acid by distilling it at 120–130° with excess of sodium polysulphate, $Na_3H(SO_4)_2$; the whole of the nitric acid then passes over, while at 230–250° the polysulphate loses all the water and can be used again.

In the Pauling electrolytic concentration process (p. 396) the anode chamber is connected above with the cathode chamber in such a way that the oxides of nitrogen formed at the cathode are passed into the nitric acid of the anode and are thus transformed into nitric acid by the oxygen evolved at the anode. According to Eng. Pat. 27,037 (1909), Pauling heats the nitric acid until a mixture of NO_2, O, and H_2O is formed and then cools rapidly to condense the water, which is separated, more concentrated nitric acid being afterwards condensed (*see also* U.S. Pat. 993,868, 1911). On the other hand, the Nobel Dynamite Company of Hamburg (Ger. Pat. 267,874, 1912) proposes to absorb the NO_2 and N_2O_3 vapours by amyl acetate, which dissolves 20 per cent. of them; these vapours are subsequently liberated in the hot by means of a gentle current of air or other gas.

---

[1] Whereas nitrous gases are readily expelled from nitric acid, they are not easily eliminated from the concentrated nitric-sulphuric acid mixtures commonly used in explosive factories, and it is best to prevent their formation during the mixing of the strong nitric acid with the sulphuric acid by cooling the mixing vessel outside with a spray of water and taking the precaution to add the sulphuric acid to the nitric acid (not vice versa) and also to stir the mass well.

FUMING NITRIC ACID. This contains much nitrogen dioxide in solution, and has an orange-yellow or brownish-yellow colour.

It is obtained by the reaction between 2 mols. of nitrate and 1 mol. of sulphuric acid at temperatures of over 200°, so that sodium sulphate is obtained together with a portion of the nitric acid in the form of NO_2. It may also be easily prepared by distilling strong commercial nitric acid with strong sulphuric acid. Industrially, however, it is obtained by the direct addition of a little starch (3–5 per cent.) to the nitrate in the retort.

It is a more energetic oxidising agent than colourless nitric acid and has a specific gravity of 1·5 to 1·54.

AQUA REGIA. This substance is obtained by mixing 1 vol. of concentrated nitric acid with 3 vols. of concentrated hydrochloric acid. It is a liquid which has the property of easily dissolving gold and platinum, because the mixture contains free nascent chlorine and nitrosyl chloride (*see above*):

$$3HCl + NO_3H = 2H_2O + Cl_2 + NOCl.$$

Neither of these acids separately dissolves the above metals.

PURE NITRIC ACID[1] is obtained by slow distillation, in a glass retort or in a flask with a small ground-in rectifying column, of 1 part of pure dry potassium nitrate (more easily obtained free from $BaCl_2$ than sodium nitrate) with 1·5 parts of pure 92–94 per cent. sulphuric acid; the first and last portions of the distillate are rejected and the middle part (about two-thirds), which passes over without red vapours, collected. If this is still slightly yellow, it is bleached by passing into it a current of dry air or CO_2 until it is decolorised. The distillation is best carried out under reduced pressure.

Pure nitric acid is obtained industrially by using pure starting materials and aspirating the vapours, evolved after one-fourth of the acid has distilled, through glass tubes and condensing them in cooled glass bottles. Pure nitric acid may also be obtained by repeated distillation of commercial concentrated nitric acid with 2–3 parts of pure sulphuric acid, first and last runnings being discarded.

APPLICATIONS. Nitric acid is employed in the manufacture of sulphuric acid (in the lead chambers) and of nitroglycerine, which is used for dynamite and ballistite. It is also used in the preparation of picric acid, guncotton, organic nitro-compounds in general (explosives and colouring matters), and ferric nitrate for dyeing. (At Lyons alone 10 tons of ferric nitrate are used daily for dyeing silk.) It is also used in the preparation of mercury fulminate, and in large quantities for the manufacture of smokeless powder, aniline dyestuffs, artificial silk, and for refining and treating the precious metals. In explosives factories the most concentrated acid (95–96 per cent.) containing less than 0·1 per cent. of nitrous acid is more especially used.

The most highly concentrated nitric acid is dispatched in iron or leaden vessels, or in glass carboys which are packed in kieselguhr (infusorial earth). It is a strongly corrosive substance and a powerful oxidising agent, and sometimes produces fires when it comes into contact with organic matter.

When large quantities of nitric acid are accidentally spilt, it is advisable not to absorb it with sand or sawdust, but to render it harmless with a powerful stream of water.

QUANTITATIVE EXAMINATION OF HNO_3. The approximate strength may be

---

[1] Impurities may be detected as follows:

Residue: 50 c.c. of the acid, evaporated on the water-bath, should leave no weighable residue.

Hydrochloric acid: 1 part of the acid dissolved in 4 parts of water, should give no opalescence with silver nitrate.

Sulphuric acid: 10 c.c. of the acid evaporated on the water-bath to 1 c.c. and this diluted with 10 c.c. of water, should give no turbidity, even after standing, with a few drops of barium nitrate solution.

Iodine and iodic acid: When the acid, diluted with 2 vols. of water, is shaken with chloroform, the latter should not be coloured, even after addition to the acid liquid of a granule of zinc.

Heavy and alkaline-earth metals: Addition of excess of ammonia, of a few drops of ammonium sulphide or of ammonium oxalate, to the dilute acid (1 : 1) should cause no change.

found from the density (*see* Table, p. 384), but for exact determinations it is necessary to titrate it (after dilution) with $\frac{N}{2}$ potassium hydroxide solution, and in order that the nitrous acid may not attack the methyl orange used as an indicator it is first poured into an excess of alkali; the indicator is then added and the excess of alkali titrated back. In the case of fuming nitric acid the strength cannot be deduced from the density by means of the Tables which we have given, because the specific gravity is increased by the dissolved N_2O_4. Thus, the quantity of this oxide dissolved in concentrated acid of 48° Bé. (1·496) may be deduced by knowing that when 1 per cent. of N_2O_4 is dissolved the specific gravity is increased by 0·0030; with 4 per cent. by 0·0252; with 8 per cent. by 0·0532; with 12 per cent. of N_2O_4 the specific gravity of concentrated nitric acid is increased by 0·0785. From the density of fuming nitric acid, by deducting the increase due to N_2O_4 (which may be determined by dropping a given volume of fuming nitric acid into a measured volume of a titrated solution of potassium permanganate) (*see* p. 381), the strength of the true nitric acid may be found from the usual Tables independently of the nitrous acid which it contains.

PRICES AND STATISTICS. Nitric acid of 36° Bé. is sold at about £12 per ton, and acid of 42° Bé., pure and free from chlorine, at £18 per ton. Chemically pure acid of 38° Bé. costs £20 per ton, of 47° Bé. £34, of 48·7° Bé. (sp. gr. 1·510) £52 per ton. Pure yellow fuming nitric acid of sp. gr. 1·480 is sold at £34, and red fuming acid of sp. gr. 1·525 (49·5° Bé.) at £42 per ton.

During the European War the price more than trebled, the nitrate that before the war cost £10 per ton rising in price in Italy to £48 per ton in 1917.

The world's output of nitric acid was 50,000 tons in 1880 (14,000 tons in the United States), 100,000 tons in 1890 (23,000 in U.S.), and about 350,000 tons in 1912.

Since 1890 the production has greatly increased on account of the large consumption for the manufacture of smokeless powder. In 1880 Germany consumed 12,585 tons of nitric acid; in 1894 it produced 54,000 tons; in 1901 about 70,000 tons, and in 1911 more than 110,000 tons; and in 1909 it exported 2138 tons. Italy produced 1990 tons of nitric acid in 1893, 2087 tons in 1903, only 1455 tons in 1905, about 2220 tons in 1906, 4800 tons in 1907, 5562 tons, of the value of £106,600, in 1908, and 9000 tons (£153,742) in 1911; the imports amounted to 10 tons in 1903, 15 in 1906, 38 in 1907, 350 in 1908, 468 in 1909, 406 in 1910, and 587 (£8927) in 1911. In the United States the production was 14,000 tons in 1880, 23,000 in 1890, 28,000 in 1902, and 50,000 in 1908. Belgium produced 10,000 tons of nitric acid at 36° Bé. (52·5 per cent.) and exported 2000 tons.

During the European War the production of nitric acid, especially in the belligerent countries, increased enormously and is calculated approximately from the probable amounts of explosives made (the numbers represent tons):

	Before the War	1915	1916
England	60,000	136,000	250,000
Germany	110,000	360,000	540,000
France	30,000	150,000	250,000
Italy	13,000	25,000	50,000
United States . . .	75,000	110,000	180,000
Russia	20,000(?)	50,000	100,000
Japan	15,000(?)	50,000	100,000
Austria	20,000(?)	100,000	180,000
Whole World . . .	350,000	1,000,000	1,675,000

PHOSPHORUS: P, 31

This element is not found free in nature on account of its great affinity for oxygen; it abounds, however, in the form of calcium phosphate as *phosphorite* (q.v.), *sombrerite*, *apatite* [$Ca_4(PO_4)_3$, CaF], and *coprolite*; it is also found as iron phosphate in *vivianite*, $Fe_3(PO_4)_2$, $8H_2O$, and as aluminium phosphate in *wavellite*, $[Al_2(PO_4)_2]_2$, $Al_2(OH)_6$, $9H_2O$; it is present to a small extent in all rocks, and therefore in all soils, of which it constitutes one of the principal fertilising factors, as it enters into the composition of the seeds of all plants.

It is of great importance for the life of vertebrate animals because it is the principal constituent (in the form of calcium phosphate) of the skeleton and the bones and enters into the composition of muscle, albuminoids, brain substance, and the nervous system (in the form of lecithin).

PROPERTIES. Distilled phosphorus, which is called *yellow* or *white phosphorus*, has the appearance of somewhat transparent white wax, and unless it is very pure has a yellowish colour; it has a specific gravity of 1·83; it is soft and can be cut with a knife, but becomes brittle at 0°; it melts at 44·4°, increasing in volume, and boils at 287°. Its specific heat is 0·188 between 7° and 13°, its heat of fusion 5 Cals. (per kilo) at 44°, and its dielectric constant 4·1 at 20°. The heat of combustion to P_2O_5 is 5900 cals. per gram. When exposed to the light it becomes brownish-yellow. It is insoluble in water, but dissolves readily in carbon bisulphide (18 : 1), from which it crystallises in rhombic dodecahedra; it is also very soluble in sulphur chloride, PCl_3, PBr_3, and CCl_4, and slightly so in alcohol, ether, benzene, xylene, methyl iodide, glycerine (0·2 per cent.), acetic acid (1 per cent. in the hot), and fused stearic acid. It is luminous and phosphorescent in the dark, probably on account of the formation of hydrogen phosphide which burns in the air. The phenomenon of phosphorescence is very complex and depends considerably on the pressure of the oxygen; it increases with rarefaction until the substance catches fire. According to the experiments of Jungfleisch (1905), Schenk, Mihr and Banthien (1906), and L. and E. Bloch (1909), the phosphorescence is explained as follows: the phosphorus first undergoes oxidation to P_2O_3, which is oxidised further with simultaneous formation of ozone, the surrounding air being ionised and the phosphorus becoming luminous in presence of even traces of oxygen.

Moist phosphorus oxidises rapidly in the air, giving white fumes of phosphorous and phosphoric acids and phosphorus pentoxide, together with hydrogen peroxide and ozone. It catches fire spontaneously in the air, forming phosphorus pentoxide (P_2O_5), especially if finely divided, as may be shown by pouring a 10 per cent. solution of phosphorus in carbon disulphide on to a sheet of paper. The carbon disulphide quickly evaporates, and the paper catches fire spontaneously. In pure dry oxygen it does not oxidise or phosphoresce and may be distilled; with increase of the partial pressure of the oxygen in mixtures with inactive gases, the phosphorescence diminishes.

If melted under water by heating to 50° and then brought in contact with a stream of oxygen, phosphorus catches fire and burns under the water; it reacts energetically with Cl, Br, and I.

If phosphorus vapours are mixed with hydrogen the gas burns with a flame which is green in the centre and is characteristic and noticeable even when only traces of phosphorus are present. In presence of minimal quantities of phosphorus, the vapours from boiling water carry off a portion of it and become phosphorescent in the dark. Mitscherlich devised an apparatus for the detection of minimal traces of phosphorus in poisoning cases by means of this reaction. The suspected substance is placed in a flask with water and boiled; the water vapour passing up the tube of the vertical condenser becomes phosphorescent in the dark if phosphorus is present. The vapours are then condensed in a solution of silver nitrate so that the presence of phosphorus may be confirmed.

Phosphorus dissolved in carbon disulphide is a strong reducing agent, and separates various metals from their salts, forming phosphides; thus, for example, it precipitates PAg_3 mixed with Ag from silver nitrate and Cu_3P_2 from copper sulphate. A stick of phosphorus immersed in copper sulphate solution becomes coated with copper. Silver nitrate may be used for healing burns caused by phosphorus. Phosphorus dissolves in a solution of caustic potash in dilute alcohol, giving a red coloration and forming polyphosphides and hypophosphites.

Phosphorus is a powerful poison, and 0·1 grm. is sufficient to cause death. In cases of phosphorus poisoning it is found absorbed in the liver (which is distended), in the blood, and in the expired air. The antidote consists of 1 grm. of copper sulphate dissolved in half a litre of water. The chronic diseases caused by phosphorus poisoning are shown amongst operatives in match factories, by necrosis of the bones and especially of the teeth and jaws.

The density of phosphorus vapour between 500° and 1000° leads to a molecular weight corresponding with P_4, and this molecule still exists in the molten state and in the cold, as may be shown cryoscopically in its solutions. Two *allotropic forms* of phosphorus other than yellow phosphorus are known, namely *red* and *black* phosphorus, which are denser and have smaller specific heats. Black phosphorus or metallic phosphorus is also called Hittorf's phosphorus, and is obtained by crystallisation from solution in molten metals; it has a specific gravity of 2·32.

PREPARATION. Phosphorus was prepared for the first time by Brand in Hamburg, and immediately afterwards by Kunkel in Wittenberg about the year 1670, by calcining the residue of evaporation of large quantities of urine in which they were seeking for the philosopher's stone (*see* p. 14).

Scheele in Sweden prepared it in 1755 from bones, and until a few years ago the same process was still used with slight modifications. Fresh bones contain 25 to 27 per cent. of phosphoric acid as tricalcium phosphate, $(PO_4)_2Ca_3$, together with considerable quantities of fat, which are extracted with benzine or carbon disulphide, and also a moderate amount of connective tissue, which may be extracted with steam and then forms the glue or gelatine of commerce.

In certain cases the bones are decomposed directly by dry distillation in iron retorts in absence of air, "Dippel animal oil" being thus obtained. *Bone charcoal* or *bone-black* remains in the retort, and after pulverisation serves as a decoloriser in many industries and especially in sugar refineries, its specific properties not being shared by wood charcoal.

In the past the bones were calcined directly in open kilns such as are used for burning lime, and were then powdered in order to obtain the so-called *bone ash*, which contains more than 50 per cent. of phosphoric acid. Until a few years ago the classic process of Nicolas and Pelletier was used. In order to obtain the bone ash, bone charcoal which has already been used for decolorising purposes is burnt in the air. 150 kilos of this ash are washed at one time in lead-lined wooden boxes with hot water and then with 150 kilos of 60 per cent. sulphuric acid. In 48 hours the whole of the tricalcium phosphate is transformed into monocalcium phosphate, which is soluble in water:

$$\text{(I)} \qquad (PO_4)_2Ca_3 + 2H_2SO_4 = 2SO_4Ca + (PO_4)_2H_4Ca.$$

It is diluted with water so that a liquid of sp. gr. 1·05 to 1·07 is obtained, the insoluble gypsum (SO_4Ca) being allowed to settle and the clear solution of monocalcium phosphate then decanted off. The water which is obtained on washing the gypsum serves for succeeding operations. The solution of the phosphate is concentrated to a sp. gr. 1·45 in large shallow leaden pans, the hot fumes from the furnace in which the bones are calcined being used for this purpose. The solution is then passed into iron pans and heated over a direct flame, a quarter of its weight of coarsely powdered wood charcoal or coke being added. When the mass is solid and contains no more than 6 per cent. of moisture, it is placed in terracotta retorts 1 metre long, in batches of 10 kilos; these retorts are placed horizontally back to back in several rows in a suitable furnace (Fig. 160). The temperature is raised in twenty-four hours to a red heat, the whole of the monocalcium phosphate being thus transformed into calcium metaphosphate:

$$\text{(II)} \qquad (PO_4)_2H_4Ca = 2H_2O + (PO_3)_2Ca.$$

Continuation of the heating to a white heat (in forty-six hours) yields tricalcium phosphate, together with carbon monoxide, which is evolved, and free phosphorus, which distils and is condensed in water in receivers, *b*:

$$\text{(III)}\qquad 3(PO_3)_2Ca + 10C = 10CO + (PO_4)_2Ca_3 + P_4.$$

The end of the reaction is indicated by the disappearance of the blue flame of CO. From 100 kilos of bone ash only about 15 kilos of very impure phosphorus, containing up to 1 per cent. of arsenic, are obtained.

As this product melts at 44°, it was formerly purified under hot water (50–60°) by filtration through porous clay plates covered with granular animal charcoal, after which it was pressed through the pores of a piece of chamois leather. Nowadays, however, it is usually re-distilled, either mixed with 15 per cent. of moist sand from cast-iron retorts, or in a current of steam and in an atmosphere of carbon dioxide.

In the works of Violet at Paris it is obtained pure and almost colourless by melting it and stirring it in water with 4 per cent. of potassium dichromate together with as much sulphuric acid. It is formed into small cylinders by running it molten into moulds also placed under water. If it solidifies slowly it remains almost transparent.

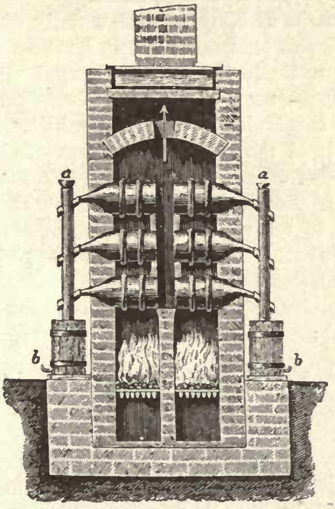


Fig. 160.

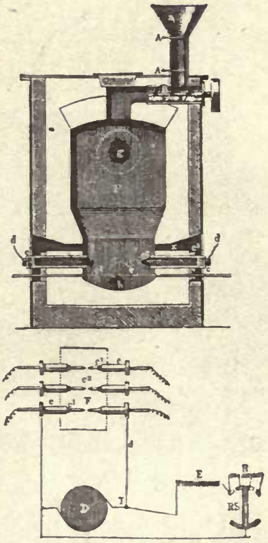


Fig. 161.

A long time ago Wöhler proposed the preparation of phosphorus from phosphatic minerals by mixing them with quartz sand (30 per cent.) and coke (10 per cent.), and then heating to a very high temperature:

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = 5CO + 3SiO_3Ca + 2P.$$

This method has been industrially employed with the help of electric furnaces proposed by Readman, Robinson, and Parker (1893), since with direct heating the calcium silicate slag strongly attacks the retorts, even when rendered more fluid by addition of soda (Claude Brisson), and the yield is only 5 per cent.; with the electric furnaces the heat is generated in the interior of the reacting mass and the yield rises to 85 per cent. The factory of Albright and Wilson (at Oldbury) alone, and its branch at Niagara Falls, prepare about 13 tons of phosphorus per month. Hempel experimented with a mixture of 5 parts of bone ash with 1·5 parts of wood charcoal and 3 parts of sand: the distillation of phosphorus began at 1200°, was in full swing at 1300°, and finished at 1450° with a yield of 92 per cent.

The process is a continuous one, the fused slag separating uninterruptedly at the base of the furnace (*h*, Fig. 161), while the finely powdered mixture of 5 parts of carbon, 5 parts of sand, and 10 parts of phosphate is introduced continuously at the top by means of a hopper, *A*, and a screw. The phosphorus fumes pass off at the top through a wide tube, *g*, and are condensed under water in copper vessels. The reaction is started by passing an electric current through thin carbons, C^2; these are afterwards removed, the arc then passing between the large carbon electrodes, *C*.

During the reaction a stream of an indifferent gas, such as coal gas, may be passed through the apparatus to prevent oxidation of the phosphorus.

According to Ger. Pat. 112,832 of the Electric Reduction Company, simple heating by means of electrical resistances is sufficient.

The Readman furnace was improved by Irvine, who used vertical electrodes and utilised the hot slag for the passage of the electric current. The Compagnie Électrique du Phosphore Billandot of Paris (Ger. Pat. 106,498) discard condensation of the hot phosphorus vapour under water owing to partial decomposition of the latter; they pass the mixture of CO and phosphorus vapour along a battery of vertical tubes inserted at top and bottom into inclined collecting tubes, by means of which the fused phosphorus at 50° separates at the base, while the CO is discharged at the top and burnt. The last traces of phosphorus vapour are retained in a tower by means of copper sulphate solution.

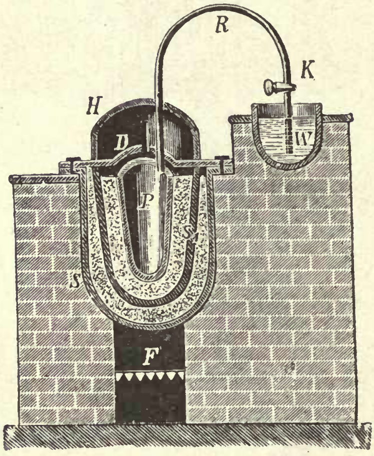


FIG. 162.

In a works at Niagara with a daily output of 85 kilos of phosphorus, 6 electric furnaces each of 50 h.p. are used, the slag discharged still containing 20 per cent. of the total phosphorus; the cost price is calculated to be 2*s.* per kilo.

In spite of the high consumption of electrical energy, most of the phosphorus produced is now made with electric furnaces, although there is a tendency to return to the retort process, using phosphoric acid and carbon, which gives first phosphorus and later, at 700–800°, phosphorus in good yield (more than 90 per cent., according to Neumann):

$$2HPO_3 + 5C = H_2O + 5CO + 2P,$$

(*see also* Harding, U.S. Pat. 602,747, and Landis, U.S. Pat. 859,086, who aim at diminishing the consumption of energy in the electric furnaces).

In 1897 Hilbert and Frank, and more recently Bradley and Jacobs, prepared phosphorus by starting from calcium phosphate and carbon only, simultaneously obtaining calcium carbide. This carbide cannot be used for the manufacture of acetylene as it contains phosphorus, but it may be used for the preparation of calcium cyanamide (*see* p. 366; also Ger. Pat. 92,838 and English Pat. 10,290, 1898): $Ca_3(PO_4)_2 + 14C = 3CaC_2 + 2P + 8CO$, or $4AlPO_4 + 19C = Al_4C_3 + 4P + 16CO$. This patent, purchased by the Comp. Électrique du Phosphore de Paris, did not give the expected results and was abandoned on this account and also because the process was not continuous. Dill obtained phosphorus by electrolysing in the hot a 65 per cent. phosphoric acid solution mixed with 20–25 per cent. of powdered carbon with a current of 80–150 amps. at 120 volts, but this process is not yet applied practically. Bonna and Leroye also suggested an electrolytic process, in which cryolite, borax, or sodium silicate is used as flux. Harding proposes to treat calcium phosphate with sulphuric acid, then to add carbon, to calcine and to treat the mass in the electric furnace.

RED PHOSPHORUS OR AMORPHOUS PHOSPHORUS. This substance was discovered by Schrötter in 1845 and was believed to be amorphous, but it has now been shown that it crystallises in the hexagonal system and is a polymeride of yellow phosphorus.

It is formed on exposing yellow phosphorus for a long period to light, or on heating it *in vacuo* or out of contact with the air at 300°. The transformation occurs at 200° if a trace of iodine is added.

It is prepared industrially in Albright's apparatus (Fig. 162), which consists of a glass or porcelain vessel, *P*, immersed in a second receiver containing sand, S_1, which is in turn heated in another sand-bath, *S*, placed directly over a furnace, *F*; the internal vessel is almost completely filled with yellow phosphorus and is then closed with a screw top, which carries a curved tube, *R*, dipping into water or mercury, *W*, and thus forms a hydraulic seal. As the whole is gradually heated the internal air escapes through the tube, which is closed after a certain time by the cock, *K*, whilst the heating is continued for 8 to 10 days at 230–250°. A mass of red phosphorus results, which is poured into water and boiled with sodium hydroxide to dissolve the last traces of yellow phosphorus which remain, PH_3 and sodium hypophosphite being thus formed. It is then further washed with water and the mass of red phosphorus is dried in stoves. Yellow phosphorus can also be easily removed with carbon disulphide, but the operation is more dangerous.

Red phosphorus consists of an apparently amorphous, bright reddish-brown powder without odour, of sp. gr. 2·19; it is not phosphorescent in the dark, does not alter in the air, and is not set on fire by friction; it is not poisonous, is insoluble in carbon disulphide, and catches fire only at a temperature above 200°; when heated rapidly to 260° in an atmosphere of carbon dioxide it is transformed into vapours of ordinary yellow phosphorus. It does not melt, even at a red heat, but already at 100° it slowly gives off vapours. When heated for a long time to 360° in sealed tubes, red phosphorus is transformed into black phosphorus, formed of rhombohedral crystals of sp. gr. 2·34.

When yellow phosphorus is transformed into red phosphorus 114 Kj. are evolved, so that the latter contains less energy and is therefore more stable and indifferent. Various catalysts have been proposed to accelerate the transformation of yellow into red phosphorus at a lower temperature, the best being phosphorus bromide and especially phosphorus iodide, which lowers the conversion temperature to about 110°.

It has been stated that shock during railway transport may change red phosphorus partly into the white form, but the rigorous experiments of A. Siemens (1906) show this to be inaccurate.

The presence of white phosphorus in the red variety may sometimes lead to trouble and may be detected by extraction with carbon disulphide. To ascertain if the phosphorus sulphide and phosphorus hydride used in making matches (*see later*) contain white phosphorus, the material is treated in a tube with a current of air, which is then caused to impinge on a charged electroscope; in presence of white phosphorus the electroscope is discharged, owing to the ionisation of the air.

Yellow phosphorus is kept under water (if the latter is free from air it will remain semi-transparent) or better under alcohol or glycerine. It is sold in this way in sealed tin-plate boxes.

USES OF PHOSPHORUS. When phosphorus is dissolved in fused stearine and the solution allowed to solidify, inscriptions luminous in the dark may be made with the material obtained. It is used also for making phosphor bronzes, but its widest application is in the manufacture of matches, although appreciable quantities are required for preparing certain aniline dyestuffs and some organic compounds. Greek fire consists of a solution of phosphorus in carbon disulphide.

The Match Industry. This is an essentially chemical industry, a product of the nineteenth century, but is to-day combined with perfect machinery which renders it one of the most interesting modern industries. The history and the early development of the match industry are so well known by everybody that we need not dwell on it in great detail. The first matches were manufactured by Chancel in Paris in 1805; they consisted of a splint of wood covered at one end with a mixture of sugar and potassium chlorate. On touching this wood with a piece of asbestos soaked in sulphuric acid fire was produced. These matches were used until about 1840, when wooden matches which lit by friction appeared. These had been discovered about 1832 almost simultaneously by the German chemist Kammerer, by the Viennese Preshel, and by the French medical man Sauria, to whom a marble monument was erected a few years ago at Saint-Lothaire, a small community in the Jura, his native country. The wooden matches had a head formed of a mixture of potassium chlorate and antimony trisulphide, held together with some kind of gum; they were lighted by rubbing them on a sheet of paper covered with powdered glass bent and stretched between two fingers. At first they were named after Congreve, an English general of artillery, who since the beginning of the century had prepared the most various and surprising rockets for use in warfare and as fireworks. Towards 1833 the discovery of Sauria and of Kammerer was introduced in a practical and convenient form in various countries simultaneously by means of wooden matches made with yellow phosphorus. As early as 1816 Derosne had attempted to prepare matches with yellow phosphorus but had not succeeded practically, and it was only much later that such were met with in the form of thin splints of wood covered at one end with sulphur, which served to transmit to the wood the flame formed at the head by a mixture of yellow phosphorus and potassium chlorate. These sulphur matches were very soon in common use in all countries, reaching even to the smallest villages, so that they were used in both the palace and the cottage.

The mixture forming the head of these sulphur matches had, however, two serious objections, which were very soon noticed also by the public, namely, that it was dangerously explosive and poisonous.

In 1837 Preshel commenced to replace the potassium chlorate by brown lead peroxide, and then by minium mixed with manganese dioxide, which was still less dangerous; one of the disadvantages was thus eliminated. There still remained, however, the danger due to the phosphorus, which had already claimed many victims through the poisoning of children who were unconscious of danger, and through the necrosis of the bones which inexorably attacked the workmen using yellow phosphorus. It was only in 1848 that Professor Böttger of Frankfort-on-Maine prepared the so-called safety matches, free from phosphorus, for the first time. In these the head contained no phosphorus, but only a mixture of substances rich in oxygen, *e. g.*, a mixture of 16 per cent. of gum, 50 per cent. of potassium chlorate, 5 per cent. of potassium chromate or calcium plumbate, 5 per cent. of sulphur, and 25 per cent. of a filling made of zinc oxide or chalk, and various colouring matters. Only in 1855 were these matches produced industrially in Lundström's factory at Jönköping (Sweden), which was started in 1845. Safety matches ignite only when they are struck on a specially prepared surface containing 50 per cent. of red phosphorus (which is not poisonous), 20 per cent. of gum, 10 per cent. of antimony sulphide, water, and inert filling material. In various countries the yellow phosphorus in matches was replaced by phosphorus sesquisulphide, P_4S_3, which is less dangerous and is used in the French State factories.[1] The Elektron Company of Griesheim has suggested the use of thiophosphites and hypothiophosphites as substitutes for phosphorus, while Wheelwright (Eng. Pat. 3214, 1910) proposed the orange-red phosphorus hydride, P_9H_2, obtained by heating the hydride, $P_{12}H_6$, at 175°.

These matches are also called Swedish matches, because it was in Sweden that they were first manufactured on a large scale, their substitution for matches containing yellow phosphorus being there enforced by law. From Sweden safety matches were imported to all the other countries, and in some of these—North America, France, England, Switzerland, and now also in Germany—laws were passed absolutely forbidding the manufacture of matches containing yellow phosphorus. Until a few years ago safety matches had the disadvantage that they could be ignited only by striking them on a specially prepared surface. Now, however, matches are prepared in France and in Switzerland with completely harmless phosphorus sulphide, and these light when struck on any roughened surface. By heating white phosphorus with phosphorus tribromide Schenck recently obtained *scarlet phosphorus*, which is merely a mixture of 70 parts of phosphorus and 30 parts of phosphorus tribromide, PBr_3; this substance is not poisonous and is more active than ordinary amorphous phosphorus, so that it is adapted for the preparation of non-poisonous matches which may be struck on any surface. In Italy safety matches

---

[1] The paste for the heads of these matches is composed of 12–13 parts of phosphorus sesquisulphide, 27–48 of potassium chlorate, 12–15 of ferric oxide, 12–18 of powdered glass, 9–12 of zinc oxide, 12–36 of gum, and 0·5 of colouring materials. It is, however, scarcely credible that all these ingredients are indispensable.

are made from ammonium thiocyanate mixed with potassium dichromate in place of yellow phosphorus (Pargotti, 1903).

The wood preferred for matches is that of the poplar (aspen), which Russia exports in large quantities, although pine and larch are also used.

The greatest advance in the match industry has occurred since 1860, when, with the help of engineers, machines were produced which enable matches to be manufactured on a large scale with a minimum amount of hand labour. From the first machine by Sebold the marvellous machines of Sévène and Cahen were gradually evolved. These perform all the necessary operations in an absolutely automatic manner. The sawing of the wood into sheets is followed by cross-cutting, which forms thousands of sticks at a single stroke, and these are arranged separately from one another in suitable frames, which then pass on to be coated with paraffin, immersed in molten sulphur, the heads covered with the inflammable mixture, dried, and finally filled automatically into the boxes, labelled and packed into cases. This is one of the examples, so frequent to-day, in which machinery is more perfect and rapid than manual labour. By means of these machines three workmen produce 500 gross boxes of matches, ready for sale, in ten hours.

Of importance in Italy is the manufacture of wax matches, formed of a few threads of cotton slightly twisted and then covered with a layer of stearine mixed with a little beeswax or paraffin wax. The head is made from paste which may or may not contain phosphorus.

The large-scale match industry gradually extended from Sweden to Russia, Austria, Germany, and later also to France and Italy. For some time competition has also arisen from new factories in America and Japan. In the whole world there are to-day more than 700 important match factories, with an annual output of about 35 milliards of boxes of the value of £12,000,000. In 1909 Sweden imported poplar wood to the value of about £68,000 (from Russia) and phosphorus to the value of £17,000. The sale of matches containing phosphorus has been prohibited in Sweden since 1901, but they may be made there for exportation. In 1860 Sweden possessed 14 match factories with 1167 workpeople and an output of the value of about £24,000; in 1909 there were 21 factories with 6800 operatives and an output of 24,700 tons of safety matches and 9000 tons of other matches, the total value being more than £800,000; the exports were nearly 20,000 tons of safety matches and 7000 tons of other matches, their value being about £640,000. The large Jönköping factory alone, with 800 workpeople, turned out a million boxes per day in 1912. Norway exported 5491 tons of matches in 1913 and 4482 tons in 1914. In 1909 England exported matches to the value of £88,000. In Germany the match industry passed from the numerous small home factories of Thuringia (400 in 1882 and only 120 in 1895) to the large works only after 1890, and in 1900 the production reached 1620 millions of boxes; in 1900 2000 tons of matches (value more than £40,000) were exported, but owing to the international competition of Japan the amount fell to 1300 tons in 1908; the consumption, which was 7 matches per day per head, rose in 1910 to 12. The Argentine has 10 large match factories, which employ 2500 workpeople and consume 700 tons of stearine annually, producing matches to the value of £400,000, of which, however, £80,000 represents the value of the boxes. In France the production in 1877 was 25,179 milliards, in 1897 33,349 milliards, and in 1907 41,369 milliards, for which 12·140 tons of red phosphorus, 31·427 tons of phosphorus sulphide, 224·127 tons of potassium chlorate, and 844·871 tons of sulphur were required; in 1912 the output was about 46 milliards, *i. e.*, 33 matches per inhabitant per day and the profit made by the State, which has a monopoly of the match trade, amounted to £1,200,000. In Brazil in 1908 425 million boxes of matches were produced. The manufacture of matches in Russia has undergone rapid changes and factories using phosphorus have disappeared; in 1902 there were 10 such factories producing almost 16 million matches, but there remained only one in 1907, with an output of 737,000; in 1902 there were 33 factories producing both phosphorus and safety matches and in 1911 only 2. The number of works making only safety matches was 83, with an output of 218 millions in 1902, and 113, with an output of 305 millions, in 1911. The Russian match exports were valued at £33,560 in 1902 (to Persia and China) and at £129,550 in 1911 (to Persia, England, Turkey, and China). Russia exports also large quantities of match sticks, produced as a domestic industry by the peasants in the Wjatka government: in 1904 the value of such exportation was £62,270, in 1909 £52,550, and in 1911 £34,350. Italy in 1903 exported 1258 tons of wooden matches (in 1908, 1541 tons valued at

£37,000) and 1610 tons of wax matches (in 1908, 1879 tons of the value £180,400). The Italian exports during recent years are as follows:

		1910	1912	1914	1915	1916	
Wooden matches	Tons:	1683	828	1241	2567	2140	(£107,015)
Stearine and wax matches, etc.	„	1852	1034	1374	1797	1226	(£159,340)

In 1910 there were in Italy 168 small and large match factories, and in 1908 the output was 41 milliards of wooden and 26·8 milliards of wax (or paraffin wax) matches; in 1910 the total output was 73 milliards and the home consumption 52 milliards (three-fourths wooden and one-fourth wax), *i. e.*, 44 matches per day per head of the population; the exportation was 5·3 milliards of wooden and 14·3 milliards of wax matches. In 1912 the State received £480,000 from the manufacturing tax. Exports go more especially to Turkey, Egypt, and Australia. In 1909 Japan exported 41,407,000 gross boxes of matches of the value of £1,200,000 (and in 1908 it exported 34,000,000 gross); 25,000 workpeople are employed in 150 works; the export forms two-thirds of the production, and 50 per cent. of it goes to China.

As regards the international trade in matches, the principal exporter is Sweden, which is followed in order by Norway, Austria-Hungary, Italy, and Russia. In the East, Japan is predominant. North and South America are protected by high customs duties. During the European War Sweden supplied many matches to England and still more to France, which also imported them from America.

Japan has during the war experienced great difficulties in obtaining a supply of phosphorus, and in 1915 it was decided to erect a phosphorus works at a cost of £100,000.

The *production of phosphorus* in 1864 in France and England was altogether 175 tons and in 1874 1200 tons; in 1880 1500 tons were produced in France and 1750 tons in England.

The world now consumes 4000 tons of phosphorus yearly in the match industry, in the preparation of aniline colours, and still more in the manufacture of very important metallic alloys, mainly prepared by new electric processes.

The most important phosphorus works are found in America (Oldbury Electro-Chemical Co. at Niagara), England, France (Lyons), and Germany (Griesheim and Frankfort); a little is produced in Sweden and in Russia. A works to manufacture amorphous phosphorus from apatite in the electric furnace was erected in Norway in 1916. A factory using wavellite (aluminium phosphate) has recently been started at Harrisburg. In 1905 Italy imported 199 tons of red and yellow phosphorus of the value of £29,850, that is, at a mean price of 3*s.* per kilo. In 1907 the imports were only 79·5 tons, in 1908 105·1 tons (valued at £14,714), in 1911 97·4 tons, in 1914 93·9 tons, in 1915 124·3 tons, and in 1916 132·5 tons (£35,776). In Italy the manufacture of phosphorus was commenced in 1917 at Monterotondo (Rome), while at Foligno the use of an electric furnace method is under investigation.

Germany imported 313 tons of phosphorus in 1901 and exported 150 tons; in 1909 it imported 178·6 tons and exported 168·5 tons, the production being about 100 tons.

The price of yellow phosphorus before the war was about 3*s.* 2½*d.* per kilo, that of red phosphorus of first quality about 5*s.* 2½*d.* per kilo, and of second quality about 3*s.*

HYDROGEN PHOSPHIDE (PHOSPHINE, PHOSPHORETTED HYDROGEN): PH_3

This substance is formed as a gas by the action of nascent hydrogen on phosphorus. It is also obtained by treating phosphonium iodide with potassium hydroxide:

$$PH_4I + KOH = H_2O + KI + PH_3.$$

It is obtained easily in less pure condition (mixed with liquid hydrogen phosphide, P_2H_4) from potassium hydroxide and phosphorus:

$$P_4 + 3KOH + 3H_2O = PH_3 + 3PH_2O \cdot OK \text{ (potassium hypophosphite).}$$

The reaction is carried out in a flask completely filled up to the stopper with a concentrated solution of potassium hydroxide (Fig. 163); two or three pieces of white phosphorus are then added, and the flask is well closed with a cork provided with a delivery tube filled with water and dipping into tepid water so that no air remains in the flask, in order to avoid the formation of the explosive mixture: $O + PH_3$. The flask is heated with a small flame and bubbles of PH_3 gas are evolved; these ignite in contact with the air as they are produced, forming rings of white smoke which enlarge as they rise in the air; the ignition in the air is due to the presence of liquid hydrogen phosphide, P_2H_4, which is formed in small quantities. If the gas is first passed through a cooled glass tube or is washed with alcohol, ether, or HCl, which absorb the P_2H_4, it no longer catches fire in the air.

PH_3, mixed with P_2H_4, is also obtained from calcium phosphide, Ca_3P_2, and HCl: $P_2Ca_3 + 6HCl = 2PH_3 + 3CaCl_2$. It is likewise obtained by heating phosphorous acid: $4PO_3H_3 = PH_3 + 3PO_4H_3$ (phosphoric acid). Calcium phosphide may now be prepared by the Goldschmidt process (1910) by heating the phosphate with aluminium powder (*see* Thermit).

Hydrogen phosphide is a colourless gas of density 1·5, with a disagreeable odour of garlic; it is very poisonous even when diluted with much air (1 to 10,000). One vol. of the gas dissolves in 5 vols. of water or in 30 vols. of saturated salt solution; the gas is slightly soluble in alcohol, ether, or oils. It is liquid at −85° (density 0·74), solid at −133·5°, and catches fire only at 100°, although oxidising agents such as HNO_3 render it spontaneously inflammable by forming P_2H_4; when mixed with oxygen it does not catch fire when pure, but ignites spontaneously with explosive violence if the pressure is diminished (*see also* p. 403). On heating or by means of the electric discharge it is decomposed into $P + H_3$. It burns with a luminous flame, forming P_2O_5. When mixed with chlorine it explodes violently: $PH_3 + 3Cl_2 = PCl_3 + 3HCl$. Wood charcoal removes and condenses the P_2H_4 and thus renders the PH_3 non-inflammable. PH_3, like phosphorus, is an anti-catalyst, retarding the decomposition of hydrogen peroxide by colloidal platinum.

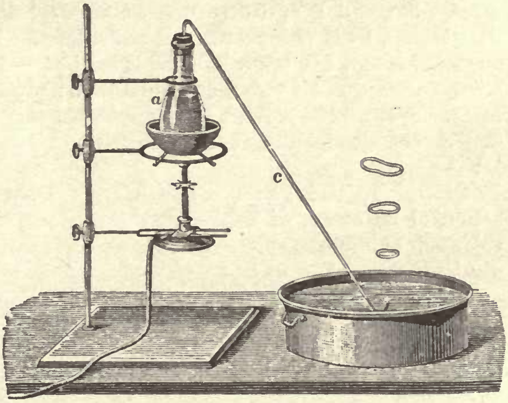


Fig. 163.

It is an energetic reducing agent and precipitates a black mixture of metal and metallic phosphide from solutions of copper sulphate or silver nitrate; by means of this reaction it may be separated from other gases. Its composition may be determined by passing a given volume of PH_3 over red-hot copper, which has been previously weighed and which combines with the phosphorus. The hydrogen which remains may then be collected and measured. It has basic properties, but these are much less marked than those of NH_3, although with dry HI or HBr it easily forms phosphonium iodide and bromide, $PH_3 + HI = PH_4I$. The group PH_4, which behaves like a metallic radical, is called *phosphonium* analogously to ammonium.

PHOSPHONIUM IODIDE forms colourless crystals which readily sublime, and is most easily obtained from P_2I_4 with a little water, that is, by adding iodine to a solution of phosphorus in carbon disulphide, evaporating the mixture and treating it with a small amount of water.

PHOSPHONIUM CHLORIDE: PH_4Cl, is formed only at − 30° or under pressure, and dissociates even at 15°. **PHOSPHONIUM BROMIDE** is solid and less stable than the iodide, but more so than the chloride: it dissociates at 30°.

LIQUID HYDROGEN PHOSPHIDE: P_2H_4. This compound is separated from PH_3 by passing the mixture obtained from calcium phosphide (*see above*) through a very cold tube. It is a colourless liquid which boils at 58° and decomposes easily, best in the light, into PH_3 and solid $P_{12}H_6$. It readily catches fire in the air.

SOLID HYDROGEN PHOSPHIDE : $P_{12}H_6$. This compound forms a yellow powder insoluble in water, which catches fire at 160–200°. Various forms of solid hydrogen phosphide are known, one of which perhaps has the formula, P_4H_2.

THERMOCHEMICAL BEHAVIOUR OF PHOSPHORUS HALIDES. Whilst such derivatives of nitrogen are pre-eminently endothermic and explosive, the phosphorus halides are exothermic, that is to say, formed with evolution of heat, and are therefore more stable. In this respect they approach more nearly to the halogen compounds of the metals. Their heat of formation diminishes with increase of the atomic weight of the halogen, and this explains how it is that PI_5 is not known and why PF_5 is a more stable compound :

$$P + Cl_5 = PCl_5 + 439 \text{ Kj. } (= 105{,}000 \text{ cals.}).$$

Also on dissolving these compounds in water much heat is developed :

$$PCl_3 + 3H_2O + aq. = PO_3H_3\,aq. + 3HCl\,aq. + 272 \text{ Kj.}$$

PHOSPHORUS TRICHLORIDE : PCl_3. This compound is obtained by passing a current of dry chlorine over gently heated phosphorus in a small flask. The phosphorus catches fire, and PCl_3 distils together with a little PCl_5, which is transformed into PCl_3 on adding a little phosphorus and redistilling. It forms a colourless liquid of pungent odour, of sp. gr. 1·6, b. pt. 76°, and is solid at — 119°. It fumes in the air because it has a great attraction for water, giving HCl and phosphorous acid : $PCl_3 + 3H_2O = PO_3H_3 + 3HCl$. It is a good solvent for phosphorus, and mixes with ether, benzene, chloroform, and carbon disulphide; it is much used in laboratories, and costs about 3*s.* 7*d.* per kilo.

PHOSPHORUS PENTACHLORIDE : PCl_5. This compound is obtained by the action of an excess of chlorine on phosphorus or by acting on PCl_3 with still more chlorine, or by passing a current of Cl into a solution of phosphorus in carbon disulphide.

It is a slightly yellow crystalline mass of irritating odour, which attacks the eyes. It sublimes without melting and when heated decomposes partially into PCl_3 and Cl_2. It melts under pressure at 148°; it fumes in moist air, since it reacts energetically with water, forming three different derivatives according to the quantity of water :

$$PCl_5 + H_2O = 2HCl + POCl_3 \text{ Phosphorus oxychloride.}$$
$$PCl_5 + 3H_2O = 5HCl + PO_3H \text{ Metaphosphoric acid.}$$
$$PCl_5 + 4H_2O = 5HCl + PO_4H_3 \text{ Phosphoric acid.}$$

Its vapour density in an atmosphere of PCl_3 corresponds with the formula PCl_5; at higher temperatures, however, it commences to dissociate into $PCl_3 + Cl_2$. At 300° dissociation is complete and the gaseous mass has a greenish colour due to the free chlorine.

PCl_5 is often used in the laboratory, especially for many reactions in organic chemistry, when the OH group is to be replaced by chlorine. It costs about 4*s.* 5*d.* per kilo.

PHOSPHORUS BROMIDES and **IODIDES** are analogous to the chlorides, and are obtained by dissolving white phosphorus in carbon disulphide and then adding the calculated quantity of bromine or iodine a little at a time; the carbon disulphide is then separated by distillation. The pentaiodide, PI_5, is not known.

Pure **PHOSPHORUS PENTAFLUORIDE** : PF_5, has been prepared by heating PCl_5 with arsenic trifluoride, $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$, and **PHOSPHORUS TRIFLUORIDE** is also known. These are more stable gases than PCl_5 and PI_3, but are extremely sensitive even to minute traces of water, which decompose them. Moissan was able to liquefy and solidify them in 1904. PF_3 melts at — 160° and boils at — 95°, whilst PF_5 melts — 83° and boils at — 75°. Phosphorus oxyfluoride boils at — 40°.

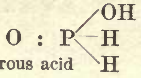
OXYGEN AND HALOGEN COMPOUNDS OF PHOSPHORUS

OXIDES

Phosphorus suboxide, P_4O. Phosphorus trioxide or phosphorous anhydride, P_4O_6 (or P_2O_3). Phosphorus tetroxide, P_2O_4. Phosphorus pentoxide or phosphoric anhydride, P_2O_5.

ACIDS

PO_2H_3 or

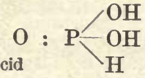


Hypophosphorous acid

PO_2H or O : P—OH

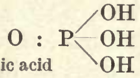
Metaphosphorous acid

PO_3H_3 or



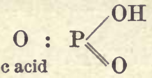
Phosphorous acid

PO_4H_3 or



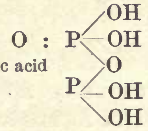
Orthophosphoric acid

PO_3H or



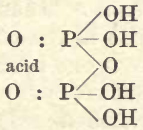
Metaphosphoric acid

$P_2O_6H_4$ or



Hypophosphoric acid

$P_2O_7H_4$ or



Pyrophosphoric acid

The oxides combine with various quantities of water to form the corresponding acids:

$$P_4O_6 + 2H_2O = 4PO_2H \text{ (metaphosphorous acid)}$$
$$P_4O_6 + 6H_2O = 4PO_3H_3 \text{ (phosphorous acid)}$$
$$P_2O_4 + 3H_2O = PO_3H_3 + PO_4H_3$$
$$P_2O_5 + H_2O = 2PO_3H \text{ (metaphosphoric acid)}$$
$$P_2O_5 + 2H_2O = P_2O_7H_4 \text{ (pyrophosphoric acid)}$$
$$P_2O_5 + 3H_2O = 2PO_4H_3 \text{ (orthophosphoric acid)}$$

Theoretically orthophosphoric acid should be $P(OH)_5$, but this compound does not exist, the phosphoric acid, PO_4H_3, ordinarily called orthophosphoric acid, being formed from it by the elimination of one molecule of water; by the elimination of a further molecule of water metaphosphoric acid is obtained.

The basicity of these acids is given by the number of hydroxyl (OH) groups which are shown in the constitutional formulæ (*see above and* p. 49), since by acting on these acids with bases only the hydrogen of the hydroxyl groups is replaced by metals with formation of salts, and not the hydrogen directly linked to phosphorus. The salts corresponding with the acids in the order in which they are given at the top of this page are called *hypophosphites, metaphosphites, phosphites, phosphates, metaphosphates, hypophosphates,* and *pyrophosphates.*

PHOSPHORUS SUBOXIDE: P_4O (PHOSPHORUS PROTOXIDE)

When white phosphorus is dissolved in potassium hydroxide, previously dissolved in aqueous alcohol, H and PH_3 are evolved, and a bright red liquid remains which on acidification deposits a gelatinous mass, composed mainly of P_4O; on filtering and repeatedly freezing, pure P_4O is obtained. It has an orange colour, is hygroscopic, and reacts with water, partially forming PH_3. At rather high temperatures it decomposes with formation of P_2O_5 and P. It is strongly attacked by halogens and by nitric acid.

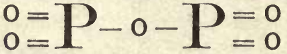
PHOSPHORUS TRIOXIDE: P_4O_6 (or P_2O_3) (PHOSPHOROUS ANHYDRIDE)

This compound is obtained when phosphorus is heated gently in a tube in a current of dry air, the phosphoric anhydride which is formed at the same time, and which is less volatile, being retained by a plug of asbestos, whilst the phosphorous anhydride condenses in a cold flask. It may also be obtained by heating phosphorous acid with phosphorus trichloride: $2PO_3H_3 + 2PCl_3 = 6HCl + P_4O_6$.

It forms white crystals united to form a wax-like mass which melts at 22·5°, easily sublimes, and boils out of contact with the air at 173°. Its vapour density leads to the formula P_4O_6; the formula P_2O_3, which was used in the past, is therefore not correct.

It dissolves in cold water, forming metaphosphorous and phosphorous acids. It reacts actively with hot water, forming red phosphorus and phosphoric acid. At about 60° it catches fire in the air, forming P_2O_5. At 400° it decomposes, giving red phosphorus and phosphorus tetroxide, P_2O_4, which forms transparent crystals yielding phosphorous and phosphoric acids with water. P_2O_4 may thus be considered as a mixed anhydride of these two acids (analogous to nitrogen tetroxide, p. 381).

PHOSPHORUS PENTOXIDE : P_2O_5 (PHOSPHORIC ANHYDRIDE)



$$\begin{matrix} O= \\ O= \end{matrix}P-O-P\begin{matrix} =O \\ =O \end{matrix}$$

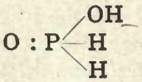
When phosphorus is burnt in iron cylinders in a current of dry air (Grabowski's continuous apparatus) a soft, white powder, consisting of P_2O_5, is formed. Its heat of formation is 370 Cals.

Since it contains also lower oxides it is purified by sublimation in a current of oxygen in presence of red-hot spongy platinum. It is known in two modifications: one is crystalline, sublimes at 250°, and, when heated to above this temperature, is transformed into the second modification, which is amorphous and volatilises only at a red heat, then condensing in the crystalline form. According to Tilden and Barnett, its vapour density indicates the molecule, P_4O_{10}.

It is odourless and extremely hygroscopic, so that it deliquesces in the air, and dissolves very actively in water, producing a hissing sound, evolving heat and being transformed into phosphoric acid. The heat of solution of the crystalline form is 40·8 Cals. and that of the amorphous variety 33·8 Cals. After exposure to the air it gives a green fluorescence (even in a vacuum) which increases in intensity at low temperatures and becomes brilliant at — 180°; the intensity gradually diminishes and the light becomes white. With HCl or PCl_5 it gives $POCl_3$. With NH_3 it forms the complex diamminopyrophosphoric acid.

It is used in many chemical operations, as it is the most energetic dehydrating agent known. It forms various acids with water (*see above*). It is placed on the market in hermetically closed vessels at a price of about 4*s*. per kilo.

HYPOPHOSPHOROUS ACID : H_3PO_2 or



$$O:P\begin{matrix} \diagup OH \\ -H \\ \diagdown H \end{matrix}$$

This is obtained by heating a concentrated solution of sodium hydroxide or lime or baryta water with white phosphorus; PH_3 is formed together with sodium, calcium, or barium hypophosphite:

$$8P + 3Ba(OH)_2 + 6H_2O = 3Ba(PO_2H_2)_2 + 2PH_3.$$

Free hypophosphorous acid is obtained from the barium salt (purified by crystallisation) with sulphuric acid; the liquid is filtered and concentrated at reduced pressure; a syrupy liquid remains which sometimes crystallises in white scales, melting at 17° (if highly purified, at 26·5°). In the hot it decomposes thus: $2PO_2H_3 = PH_3 + PO_4H_3$.

It has a great affinity for oxygen, which transforms it into phosphoric acid, so that it is a strong reducing agent; thus it reduces H_2SO_4 to SO_2, and then to sulphur; it separates metals (gold, silver, mercury) from certain of their salts in solution; it precipitates copper hydride, Cu_2H_4, when heated with copper sulphate, $CuSO_4$, and by this means is distinguished from phosphorous acid. By nascent hydrogen it is reduced to PH_3.

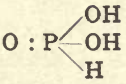
It is a monobasic acid, since the molecule contains only one ionic hydrogen atom replaceable by metals. The electrolytic dissociation diminishes in extent as the temperature rises, so that dissociation into ions occurs with absorption of heat; thus, the acid behaves as an endothermic substance. This abnormality explains also the high value of the heat of neutralisation—about 15,500 Cals., whereas for strong acids the value is 13,500 Cals. and for weak acids lower still. Other acids with a negative heat of ionisation, such as hydrofluoric and phosphoric acids, behave similarly. The heat of formation of hypophosphorous acid from the elements is 140 Cals. (in presence of water only 27·3 Cals.).

The salts, termed hypophosphites, are soluble in the air (even those of the heavy metals) and readily undergo change into phosphites and phosphates in the air. The hypophosphites evolve PH_3 when heated and with ammonium molybdate they give a blue coloration (whereas phosphates give a yellow precipitate); barium or calcium chloride precipitates phosphites or phosphates, but not hypophosphites; the latter, however, separate gold and silver from their salts. The hypophosphites (of Na and Ca) are used in medicine and should be completely soluble in water and free from phosphites (poisonous); they cost about 5*s.* 6*d.* per kilo.

METAPHOSPHOROUS ACID, HPO_2 or $O:P—OH$

This compound is formed in slender crystals, m.pt. about 80°, by the slow oxidation of phosphine at reduced pressure: $PH_3 + O_2 = H_2 + PO_2H$. It is also obtained from phosphorous anhydride with a little water. It is transformed by steam into phosphorous acid.

PHOSPHOROUS ACID, H_3PO_3 or



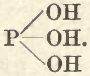
$$O:P\left<\begin{array}{l}OH\\OH\\H\end{array}\right.$$

This compound is obtained by the careful addition of phosphorus trichloride, with cooling, to water: $PCl_3 + 3H_2O = 3HCl + PO_3H_3$; the solution thus obtained is evaporated *in vacuo*, a colourless crystalline rather hygroscopic mass, readily soluble in water, then remaining. It melts at 71°, and is decomposed at higher temperatures into phosphoric acid and phosphine, $4PO_3H_3 = PH_3 + 3PO_4H_3$. Its heat of formation from the elements is 227·7 Cals.

It is also formed, together with a little phosphoric acid, hypophosphoric acid and ozone, by the slow oxidation of white phosphorus in moist air.

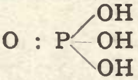
It is a strong reducing agent, as it abstracts oxygen from air and water, in presence of halogens, with formation of phosphoric acid. It precipitates the metals from solutions of silver nitrate, gold chloride, and mercuric chloride (difference from phosphates); it differs from hypophosphorous acid by not reacting with copper sulphate.

Since it contains two hydroxyl groups it is a dibasic acid and forms two classes of salts: *neutral* and *acid phosphites*, two hydrogen atoms being replaced by metals in the former and one only in the latter. The phosphites differ from the hypophosphites by not being oxidised by the air, but are oxidised by strong oxidising agents. They separate metals from certain salts in the same way as phosphorous acid. When heated to redness they form hydrogen, pyrophosphates, and metallic phosphides. The alkali phosphites and those of calcium and barium are insoluble in water (dissolved by alkali); the acid phosphites are soluble.

With nascent hydrogen phosphorous acid forms PH_3. Certain compounds are known in which phosphorous acid appears to have a symmetrical constitution  $P\left<\begin{array}{l}OH\\OH\\OH\end{array}\right.$.

Pure calcium or sodium phosphites cost 12*s.*–16*s.* per kilo.

PHOSPHORIC ACID, H_3PO_4 (ORTHOPHOSPHORIC ACID)



$$O:P\left<\begin{array}{l}OH\\OH\\OH\end{array}\right.$$

This acid is abundant in nature in the form of phosphates. It is obtained in the laboratory by dissolving P_2O_5 in hot water: $P_2O_5 + 3H_2O = 2PO_4H_3$, or by decomposing phosphorus pentachloride with water:

$$PCl_5 + 4H_2O = 5HCl + PO_4H_3.$$

It is also obtained from phosphorus oxychloride and water:

$$POCl_3 + 3H_2O = 3HCl + PO_4H_3.$$

It is prepared industrially by decomposing bone ash (tricalcium phosphate) in the hot with the calculated quantity of dilute sulphuric acid:

$$(PO_4)_2Ca_3 + 3H_2SO_4 = 3CaSO_4 + 2PO_4H_3;$$

the mass is filtered and the filtrate concentrated, the rest of the dissolved lime being precipitated with a little sulphuric acid and filtered off and the liquid strongly heated to expel the excess of sulphuric acid. It is obtained in a purer form by heating 1 part of yellow phosphorus with 16 parts of nitric acid and a trace of iodine, evaporating the solution in a platinum dish and oxidising the last traces of phosphorous acid by means of nitric acid; the acid then remains as a syrup, which solidifies when seeded with a small crystal.

When free from water it forms colourless prismatic crystals deliquescent in the air, which melt at 38·6°; it is very soluble in water, and the solution, which is strongly acid, evolves hydrogen with various metals. When it is heated to 200° to 300° water is evolved and pyrophosphoric acid, $H_4P_2O_7$, formed, together with a little metaphosphoric acid. When heated to above 400° it is all transformed into metaphosphoric acid in a vitreous condition.

Phosphoric acid contains three H cations, and is thus tribasic, forming three series of salts (*see* Part III, Calcium Phosphate, etc.). Thus we have:

NaH_2PO_4, *primary* sodium phosphate, monosodium phosphate, also called acid sodium phosphate;

Na_2HPO_4, *secondary* sodium phosphate, or disodium phosphate, which is the ordinary laboratory preparation, called the neutral phosphate;

Na_3PO_4, *tertiary* sodium phosphate, or trisodium phosphate, also called basic phosphate.

All the alkali phosphates and the primary phosphates in general are soluble in water and give a yellow precipitate of silver phosphate, Ag_3PO_4, with silver nitrate. This precipitate is soluble in ammonia and in nitric acid; the other phosphates of the alkaline earths are insoluble in water.

Magnesium salts, in presence of ammonia, precipitate phosphoric acid or soluble phosphates in the form of magnesium ammonium phosphate:

$$MgSO_4 + PO_4HNa_2 + NH_3 = SO_4Na_2 + Mg(NH_4)PO_4$$

(with $6H_2O$ of crystallisation).

The yellow precipitate formed by ammonium molybdate with phosphoric acid or phosphates in presence of nitric acid at a temperature of about 60°, is also of analytical importance; the product has the formula: $PO_4(NH_4)_3, 11MoO_3 + 6H_2O$ = *ammonium phosphomolybdate.*

Phosphoric acid is used in the preparation of various phosphates and also of hydrogen peroxide. The crude acid in paste form (48 to 50 per cent.) costs about £20 per ton; the commercially pure liquid acid of 44° Bé. (40 per cent.) costs £14; the chemically pure solution of 34° Bé. costs 1*s.* 1½*d.* per kilo, that of 63° Bé. 2*s.*, and the crystallised solid 3*s.* 3*d.* per kilo.

Italy imports about 8 tons of the value £260 per annum.

METAPHOSPHORIC ACID, HPO_3 or $O : P\langle{}^{OH}_{O}$

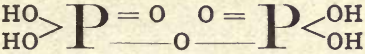
This compound is formed by heating phosphoric acid to redness; it is also easily obtained by treating phosphorus pentoxide with the calculated quantity of water: $P_2O_5 + H_2O = 2PO_3H$, or by heating diammonium phosphate: $(NH_4)_2HPO_4 = 2NH_3 + H_2O + PO_3H$.

It forms a transparent glassy mass which melts on heating, and evaporates without decomposition. It is the most stable and the most energetic at high temperatures of the oxy-acids of phosphorus. It is very soluble in water and therefore very hygroscopic. It is distinguished from ortho- and pyro-phosphoric acids by its property of coagulating an aqueous solution of albumen. The aqueous solution of metaphosphoric acid is transformed at ordinary temperatures into orthophosphoric acid : $HPO_3 + H_2O = PO_4H_3$.

It contains a single atom of hydroxylic hydrogen and is thus a monobasic acid. Its salts are called metaphosphates and are prepared by heating the primary orthophosphates : $PO_4NaH_2 = H_2O + PO_3Na$. The reverse reaction is obtained on heating the metaphosphates with water. It forms a white precipitate with barium or calcium chloride, thus differing from pyrophosphoric acid.

Metaphosphoric acids, and corresponding salts, are known which are formed by the polymerisation of two or more molecules of ordinary metaphosphoric acid; there appear to be well-defined di-, tri-, tetra-, and hexa-metaphosphoric acids : $[HPO_3]n$.

PYROPHOSPHORIC ACID, $H_4P_2O_7$ or



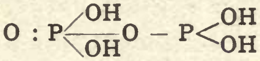
$$\frac{HO}{HO}{>}P{=}O \quad O{=}P{<}\frac{OH}{OH}, \quad P{-}O{-}P$$

This acid is obtained by heating orthophosphoric acid to over 210°, with separation of water : $2PO_4H_3 - H_2O = P_2O_7H_4$. A little metaphosphoric acid is, however, always formed at the same time, so that it is better to prepare pyrophosphoric acid by heating disodium phosphate : $2PO_4HNa_2 = H_2O + P_2O_7Na_4$; the sodium pyrophosphate is dissolved in water and precipitated with a soluble lead salt, the lead being then eliminated with H_2S and the solution filtered. On concentrating the solution of the free acid *in vacuo* a white crystalline mass remains, which is very soluble in water; in course of time the aqueous solution is transformed into orthophosphoric acid.

It is a tetrabasic acid, and its salts are called pyrophosphates. However, only two series of salts are known, the di- and tetra-substituted salts; these are stable, and regenerate the normal phosphates only under the action of mineral acids.

Pyrophosphoric acid is distinguished from phosphoric acid by giving a *white* precipitate of silver pyrophosphate with silver nitrate. It does not coagulate egg albumen, and is not precipitated by barium chloride, differing in these respects from metaphosphoric acid.

HYPOPHOSPHORIC ACID, $H_4P_2O_6$ or



$$O : P{<}\begin{matrix}OH\\ \text{---}O - P{<}\frac{OH}{OH}\\ OH\end{matrix}$$

This compound may be considered to be formed by the dehydration of one molecule of phosphoric acid and one molecule of phosphorous acid :

$$\left\{\begin{matrix}PO_3H_3\\PO_4H_3\end{matrix}\right. - H_2O = P_2O_6H_4.$$

It is obtained by the slow oxidation of moist white phosphorus in the air, together with phosphorous and phosphoric acids, from which it may be separated by neutralising the mixture with NaOH, because it forms a sodium salt, $P_2O_6Na_2H_2 + 6H_2O$, which crystallises well, and is only slightly soluble in water; with aqueous barium chloride insoluble barium hypophosphate is obtained, which is then decomposed with dilute sulphuric acid; on filtering, a stable solution of free hypophosphoric acid is obtained. At temperatures below 30° it may be obtained also in crystals. At high temperatures it is decomposed into phosphoric and phosphorous acids. It is distinguished from phosphorous acid by not reducing metallic salts. It is a tetrabasic acid, as it contains four atoms of hydroxylic hydrogen and four series of salts are known.

The following characteristic reactions suffice to distinguish ortho-, pyro-, and metaphosphoric acids one from another. Of the aluminium and chromium salts only the orthophosphates are soluble in acetic acid. Cobalt meta- and pyro-phosphates have a red colour and are soluble in excess of the same phosphates, but insoluble in acetic acid; cobalt orthophosphate, on the other hand, is blue, insoluble in excess of orthophosphate, but soluble in acetic acid; in this way even traces of orthophosphoric acid may be detected in presence of the other two acids. Alkaline solutions of bismuth (and also amminocobaltic solutions) form a precipitate only with metaphosphates, soluble in excess of metaphosphate.

With copper salts the pyrophosphates alone give a precipitate, which is soluble in excess of pyrophosphate; the ortho- and meta-phosphates are not precipitated by copper salts.

VARIOUS PHOSPHORUS DERIVATIVES

PHOSPHORUS OXYCHLORIDE, $POCl_3$. This compound may be considered as a chloride of orthophosphoric acid, in which the three hydroxyl groups are replaced by three atoms of chlorine. It is produced by treating phosphorus pentachloride with a little water: $PCl_5 + H_2O = 2HCl + POCl_3$, or preferably by distilling PCl_5 either with phosphorus pentoxide: $3PCl_5 + P_2O_5 = 5POCl_3$, or with boric acid:

$$3PCl_5 + 2BO_3H_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

By the action of ozonised air on phosphorus trichloride, the oxychloride is also formed, by direct addition of one atom of oxygen:

$$PCl_3 + O_3 = POCl_3 + O_2.$$

Potassium chlorate also reacts energetically with phosphorus trichloride:

$$3PCl_3 + ClO_3K = 3POCl_3 + KCl.$$

It is a colourless liquid which fumes strongly in the air, of sp. gr. 1·68; it boils at 107° and solidifies below 2°.

It is decomposed by water into meta- and ortho-phosphoric acids:

$$POCl_3 + 2H_2O = PO_3H + 3HCl,$$

or with much water: $POCl_3 + 3H_2O = PO_4H_3 + 3HCl$.

Phosphorus oxychloride is also prepared by distilling 1 part of dry oxalic acid with 2 parts of PCl_5. It costs about 4*s*. 6*d*. per kilo.

By means of NH_3 the chlorine in $POCl_3$ may be replaced step by step by ammoniacal residues, and one thus obtains, for example, $\underset{\text{Chlorophosphoric amide}}{POCl_2 \cdot NH_2}$ and $\underset{\text{Phosphoric triamide}}{PO(NH_2)_3}$; aminophosphoric acid, $O : P{<}\begin{matrix}(OH)_2\\ NH_2\end{matrix}$, and diaminophosphoric acid, $O : P{<}\begin{matrix}OH\\ (NH)_2\end{matrix}$, phosphamide, $O : P{<}\begin{matrix}NH_2\\ NH\end{matrix}$, phospham, $P_3H_3N_6$, etc., are also known.

PHOSPHORUS SULPHOCHLORIDE, $PSCl_3$. This compound is of analogous composition to the oxychloride, and is obtained by heating phosphorus trichloride with sulphur at 130°, or by the following reaction: $PCl_5 + H_2S = PSCl_3 + 2HCl$.

It forms a colourless liquid, which boils at 124° to 125°, of sp. gr. 1·6. It is decomposed by water, forming phosphoric acid, hydrochloric acid, and hydrogen sulphide.

PHOSPHORUS TRISULPHIDE and PENTASULPHIDE, P_2S_3 and P_4S_{10}. These compounds are obtained by the direct interaction of sulphur and red phosphorus; with white phosphorus explosions easily occur. They are yellow crystalline compounds; the former boils at 540°, while the latter boils at 520° and melts at 275°. With water they form H_2S and phosphorous and phosphoric acids respectively. P_2S_3 is to-day used in large quantities for the manufacture of safety matches which may be struck on any surface.

The molecular magnitude of the pentasulphide, determined (in 1910) in carbon disulphide solution, is P_4S_{10}.

P_4S_{10} is often employed for the preparation of various organic products (thioesters, etc.); with potassium sulphide it forms potassium thiophosphate, K_3PS_4.

PHOSPHATES, SUPERPHOSPHATES, and CHEMICAL FERTILISERS (*see* Part III).

ARSENIC: As, 74·96

Arsenic is contained in various minerals which have been known since ancient times, and Gebir clearly described arsenic oxide, which he obtained by burning arsenic sulphide. Brandt in 1773 knew metallic arsenic.

Arsenic is found in nature in the free state as a mineral, but more abundantly combined in the form of sulphides (realgar, As_2S_2; orpiment, As_2S_3) or arsenical pyrites, FeSAs, and smalt or mispickel, CoSAs.

It is found in small quantities in many mineral waters (for instance, in the waters of Roncegno), where it was found for the first time by Will and then by Fresenius.

It is obtained by heating AsFeS out of contact with the air; the arsenic sublimes and iron sulphide remains. Also, as in the case of the metals, it is obtained by heating arsenious oxide (formed by roasting the sulphide in the air) in presence of carbon:

$$As_2O_3 + 3C = 3CO + As_2.$$

According to Ger. Pats. 142,932 (1900), 195,465 (1903) and 214,814 (1908), the continued heating of the furnace may be dispensed with if a current of air is injected immediately the sulphur begins to burn, the combustion being thus maintained.

Attempts have been made to prepare it electrolytically, solutions being prepared, as with antimony (*see later*), in alkaline sulphides (Siemens & Halske system; *see also* U.S. Pat. 927,021, 1909). A more practical process than this is that of Westmann (Eng. Pat. 17,027, 1900), who heats the arsenic-rich ore in an electric furnace with ferrous sulphide and sublimes in an atmosphere of nitrogen; large 1000-kilowatt-hour furnaces are used taking 1 ton of the ore.

Arsenic crystallises in the hexagonal system and has a specific gravity of 5·73.

It is known in various crystalline forms and also in the amorphous state, but in reality the latter variety is an agglomerate of microscopic crystals of the regular system. True *amorphous arsenic* is, however, also known and is obtained by distilling arsenic in a current of hydrogen; this product has a blackish and but slightly lustrous aspect and a specific gravity of 4·7, and on heating to 360° it is transformed into crystalline arsenic with evolution of heat. When heated with a solution of sodium hypochlorite it acquires a lustrous metallic aspect; thus, also, if heated with a trace of iodine it forms arsenic iodide, which evaporates immediately, leaving lustrous crystalline arsenic behind.

A new form has recently been prepared, namely, *yellow arsenic*, by distilling black arsenic *in vacuo* at 450° in a dark chamber with a red light. The vapours which distil are condensed in a vessel surrounded with liquid air. Under the action of light or heat it is immediately transformed into black arsenic.

When arsenic is heated in an indifferent gas such as CO_2 at 450° it sublimes without melting, but when exposed to strong pressure and heated in closed tubes it melts. The vapours of arsenic are yellowish, and the vapour density indicates a tetratomic molecule, As_4. At 1700° it dissociates into diatomic molecules, As_2. In the air it catches fire at 180°, burning with a faintly blue flame and giving off an odour of garlic with formation of arsenious oxide, As_2O_3. When gently heated under the influence of light, yellow arsenic, As_4, is first transformed into brown arsenic As_2, and then into metallic arsenic As, which is monatomic and a conductor of electricity. Another form of arsenic, As_8, insoluble in the various solvents, also appears to exist. Yellow arsenic, on the other hand, dissolves in carbon disulphide (8 per cent. at 20° and 11 per cent. at 45°) and has a distinct alliaceous odour. Arsenic ignites in an atmosphere of chlorine and, like sulphur, unites with various metals; in its other properties it more closely resembles nitrogen, although it has also certain metallic characters. The metallic sulphides and arsenides are isomorphous, and the sulphur and arsenic replace one another atom for atom (*e.g.*, FeS_2, FeAsS, $FeAs_2$), in spite of the fact that sulphur is divalent and arsenic trivalent.

Metallic arsenic is now used only for making small shot, and when pure and crystalline costs £3 8*s*. per cwt.; the commercial product (80 per cent.) costs £2 16*s*. per cwt.

Germany produced 4913 tons of arsenic minerals in 1905, and Italy 451 tons, worth £1010, in 1908, and 16 tons in 1910. Italy imported 5·5 tons in 1911, 3·5 in 1914, and 2·7 (£260) in 1916. France exported 1351 tons of arsenic minerals in 1913 and 1346 tons in 1914, and imported 11·4 tons of metallic arsenic in 1913 and 11·3 tons in 1914.

HYDROGEN ARSENIDE (ARSENURETTED HYDROGEN, ARSINE): AsH_3

This gas was discovered by Scheele in 1755 and is always obtained when a mineral acid such as HCl or H_2SO_4 acts on metallic zinc mixed with arsenic compounds. The nascent hydrogen which is formed unites with the arsenic: $As_2O_3 + 6H_2 = 3H_2O + 2AsH_3$.

It is also obtained from an alloy of Zn and As or of Na and As on treating it with HCl or H_2SO_4, thus: $As_2Zn_3 + 6HCl = 3ZnCl_2 + 2AsH_3$.

It is a powerful poison, and the chemists, Gehlen in 1815, Bullacke, and recently Schulze at St. Jago, who worked with it without proper precautions, died after prolonged agonies through having breathed it in small quantities. Bunsen recommended fresh ferric hydroxide, prepared by precipitating a soluble ferric salt with magnesia, as an antidote. It has a repugnant odour of garlic; it is liquid at − 55°. When ignited it burns in the air with a pale bluish flame forming arsenic trioxide, As_2O_3. At a red heat or under the action of the electric discharge it decomposes into As and H; thus, by passing a current of AsH_3 through a glass tube which is heated at a certain point with a flame a black shining deposit of arsenic (mirror) is formed, and thus also, if a cold body such as a porcelain dish is placed in the flame of H and AsH_3, shining spots of arsenic are deposited on the dish. Arsenic hydride has less basic chemical properties than hydrogen phosphide, so that it does not combine with the halogen hydracids, whilst it has a tendency to combine with metallic salts, forming metallic arsenides. Thus, for example, with a concentrated solution of silver nitrate it gives a yellow precipitate, $AsAg_3, 3AgNO_3$, from which on dilution with water black metallic silver separates, arsenious acid and nitric acid being also formed (Gutzeit's reaction):

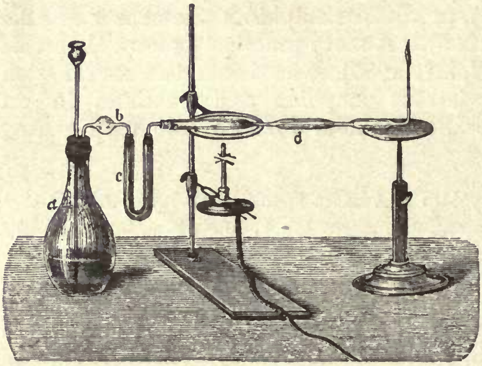


FIG. 166.

(*a*) $AsH_3 + 3AgNO_3 = 3HNO_3 + AsAg_3$ (Reckleben, 1909).

(*b*) $AsAg_3 + 3AgNO_3 + 3H_2O = 3HNO_3 + AsO_3H_3 + 6\ Ag$.

This reaction of Gutzeit is extremely delicate and is used for the detection of arsenic, as 0·001 mgrm. of As_2O_3 can still be detected; it is carried out as follows: A portion of the substance to be tested is placed in a test-tube and zinc and sulphuric acid are added; the test-tube is then loosely closed with a little cotton wool in order to retain any spray, and its mouth is covered with a strip of filter-paper on to which a drop of a 50 per cent. solution of silver nitrate is poured. In the presence of even minimal traces of arsenic the filter-paper acquires a yellow colour which turns to black on washing with water.

Since the same reaction is given by H_2S and by PH_3 it is necessary first to oxidise the substance by heating with HCl and potassium chlorate if there is any chance of these substances being formed.

By means of these reactions it is easy to detect even the smallest traces, even down to 0·01 mgrm. of arsenic, especially in poisoning cases, by introducing the substances into Marsh's apparatus (Fig. 166). This is formed of a flask, *a*, which contains pure zinc and pure dilute H_2SO_4 free from arsenic. The nascent hydrogen developed forms volatile AsH_3 with arsenic compounds, this being dried in a calcium chloride tube, *c*, and passed through the tube *d*, which is drawn out at more than one point. This tube is then heated in front of the constriction, by which means AsH_3 is decomposed and deposits metallic arsenic in the drawn-out portions, in the form of black shining mirrors.

It is necessary to drive out all the air from the apparatus before heating, and the hydrogen at the end of the tube may then be kindled (*see* p. 136).

The black mirror which is formed in the capillary tube, *d*, or on the porcelain capsule introduced into the hydrogen flame, may be distinguished from similar spots formed of antimony, because the spots due to arsenic are soluble in sodium hypochlorite, whilst those due to antimony are not.

The compound, As_2H_4, analogous to P_2H_4 is not itself known, but its organic derivatives are known, for example, the organic derivatives of *cacodyl:* $(CH_3)_2 : As \cdot As : (CH_3)_2$, which have an extremely repugnant odour and are obtained on heating potassium acetate to redness with arsenious oxide; cacodyl oxide is formed and serves for the recognition of small quantities of arsenic owing to its characteristic odour.

SOLID HYDROGEN ARSENIDE : As_4H_2, is known as a brown powder, which is formed from AsH_3 in the presence of nitric acid.

ARSENIC SULPHIDES : As_2S_2, As_2S_3, As_2S_5

These are formed directly from the elements; the two latter are also obtained from the arsenic oxides with H_2S (in which particular arsenic behaves as a metal :)

$$As_2O_3 + 3H_2S = 3H_2O + As_2S_3; \quad As_2O_5 + 5H_2S = 5H_2O + As_2S_5.$$

ARSENIC DISULPHIDE : As_2S_2. This compound is found in nature as a mineral, *realgar,* and forms ruby-red, translucent crystals of sp. gr. 3·5. Together with arsenic, it is sometimes found mixed with lead and silver minerals in Hungary, Transylvania and Bohemia, and on Vesuvius. It is prepared by melting together the calculated quantities of As and S, and then has the sp. gr. 2·3–3·3. Its vapour density below 900° corresponds with the formula As_4S_4 and above 900° with As_2S_2.

It was used in painting, but its use has now been abandoned, as it is poisonous. It is used for fireworks, in the manufacture of shot, in calico printing (as a reducing agent for indigo), and also for removing the hair from hides. It costs about £40 per ton.

ARSENIC TRISULPHIDE : As_2S_3. This compound also is found in nature as the mineral *orpiment,* in yellow, crystalline, scaly lustrous masses of sp. gr. 3·46—in the Tyrol, in the *solfatare* of Naples, in the dolomites of St. Gothard, in Banato (Hungary), in Persia, and in the lignites of China and Japan. Arsenious acid or arsenites in acid solution form with H_2S an amorphous, deep yellow or reddish precipitate of As_2S_3 insoluble in water (when just formed it dissolves slightly in the colloidal state) or in acids, but soluble in alkalies or alkali sulphides; when melted it yields a product which resembles orpiment, but has the sp. gr. 2·7. It is prepared industrially by fusing together As_2O_3 and sulphur. When subjected to prolonged boiling with HCl it yields volatile $AsCl_3$. It is largely used as an oil paint, the brightness of the colour depending on the fineness of grinding. It boils above 700° and dissociates at 1000°. It serves for the reduction of indigo and to some extent as a depilatory, but the amount now used is small, the price being about £38 per ton. France imported 259 tons in 1913, 163 tons in 1914, and 3·6 tons in 1915.

ARSENIC PENTASULPHIDE : As_2S_5. This compound is formed, together with a little As_2S_3, on passing a copious stream of H_2S through an acid solution of arsenic acid or of an arsenate at 80° : $2AsO_4H_3 + 5H_2S = As_2S_5 + 8H_2O$; under other conditions, however, H_2S reduces arsenic acid to arsenious acid, with separation of sulphur. It is also obtained by melting the disulphide with sulphur; also, as a pale yellow powder, by treating sodium thioarsenate, AsS_4Na_3, with an acid. It is insoluble in water and acids, and has a lighter colour than the trisulphide. At about 500° its vapours dissociate into $As_2S_3 + S_2$. It dissolves in alkalies or alkali sulphides, with formation of thioarsenates or sulphoxy-arsenates.

THIOSALTS OF ARSENIC

These compounds are formed from arsenic sulphides (which may be considered as thioanhydrides) by dissolving them in alkali sulphides :

$$As_2S_3 + 3K_2S = 2AsS_3K_3; \quad As_2S_5 + 3K_2S = 2AsS_4K_3.$$

They are also obtained from arsenates with H_2S:

$$AsO_4K_3 + 4H_2S = 4H_2O + AsS_4K_3.$$

The alkali sulphosalts form crystals soluble in water, whilst those of the other metals are insoluble. On attempting to obtain thioarsenious or thioarsenic acid by the action of HCl, decomposition occurs with separation of As_2S_5 and H_2S.[1]

CHLORIDES AND IODIDES OF ARSENIC

ARSENIC TRICHLORIDE : $AsCl_3$. This compound is formed on burning arsenic in a current of chlorine, even at low temperatures. It is prepared by adding dry sodium chloride to a hot solution of As_4O_6 and concentrated H_2SO_4; the trichloride distils and is then condensed in an efficient refrigerator in the form of an oily, colourless, fuming, and very poisonous liquid of sp. gr. 2·205 at 0° and 2·167 at 20°. When pure and free from chlorine it solidifies at $-18°$, and boils at 130·2°. The formula As_2Cl_6 has also been attributed to this compound. It dissolves in chloroform, carbon tetrachloride, benzene, oils, etc.

In contact with water it is partially decomposed into oxide and HCl until a definite equilibrium is established; this depends on the concentrations of the substances present, the reaction being reversible:

$$4AsCl_3 + 6H_2O \rightleftarrows As_4O_6 + 12HCl.$$

The presence of sulphuric acid is necessary for the formation of arsenic trichloride from sodium chloride and As_4O_6, in order to combine with the water and prevent the reverse reaction. As_4O_6 is also transformed into $AsCl_3$ by an excess of HCl. Since $AsCl_3$ is volatile on heating, whilst the oxide is not, it is not permissible, during chemical analysis, to evaporate solutions of the oxide in presence of HCl; in order to avoid loss of arsenic the solution is either made alkaline or oxidised with chlorates or nitric acid, because arsenic acid is then formed on heating, and cannot yield the corresponding pentachloride or any other volatile chloride, even in presence of much HCl. These facts are utilised in the elimination of arsenic from sulphuric acid (*see* p. 311), the arsenic being reduced to the state of arsenious acid with sulphur dioxide and a current of HCl then passed into the hot acid, thus rendering the arsenic volatile in the form of $AsCl_3$. The reverse process is also used in the *purification of hydrochloric acid* by oxidising the arsenic which it contains (*see* p. 179) and then distilling it. Pure hydrochloric acid then passes into the distillate, whilst the arsenic acid remains behind.

The heat of formation of $AsCl_3$ is 713 Cals.; the commercial product costs 12*s.* per kilo.

ARSENIC PENTACHLORIDE $AsCl_5$. This compound is probably formed by the action of dry chlorine on $AsCl_3$ at $-60°$. It forms yellow crystals which melt at $-40°$ and are soluble in ether; it begins to decompose at $-28°$ and at the ordinary temperature it is completely decomposed into $AsCl_3 + Cl_2$. Some of its organic derivatives are more stable.

---

[1] Sulpharsenates or thioarsenates are formed also from the pentasulphide and an alkali sulphide, from the trisulphide and an alkali polysulphide, or by fusing the dry pentasulphide with a solid alkali hydroxide or carbonate. Three series of these salts (but not the corresponding free acids) are known: orthothioarsenates, AsS_4X_2; pyrothioarsenates, $As_2S_7X_2$; and metathioarsenates, AsS_3X, where X represents a monovalent metal.

Sodium thioarsenate forms crystals of the formula, $AsS_4Na_3 + 8H_2O$. The alkaline sulphosalts are soluble in water, and with salts of heavy metals yield precipitates of the sulpho-salts of the heavy metals, which have various colours (calcium and barium salts, white; copper, grey or reddish-brown; nickel, cobalt, and iron, brown; mercury, green to black; most other metals, yellow). Treatment of silver nitrate solution with excess of thioarsenate yields silver sulphide, whereas if the silver nitrate is poured slowly into the thioarsenate in presence of potassium cyanide, sulphur separates and proustite, AsS_3Ag_3, is formed.

Sulphoxyarsenates: mono-, di-, and tri-sulphoxyarsenates, AsO_3SX_3, $AsO_2S_2X_3$, and $AsOS_3X_3$, are known, and the first two may be separated one from the other by means of the strontium salts, the mono-salt being only slightly, and the di-salt readily, soluble in water; the latter may be afterwards precipitated as barium salt. In aqueous solution trithioarsenates are dissociated and yield a mixture of numerous sulpho- and sulphoxy-arsenates. When solutions of sodium sulphide and arsenic trioxide in the proportion $2Na_2S : As_2O_3$ are mixed, a considerable amount of arsenic is precipitated, while the filtrate afterwards deposits a mass of crystals composed of sodium arsenate and various sulphoxyarsenates. The sulphoxyarsenates are mostly colourless, only the complex sodium salt, $As_{18}O_7S_{24}Na_8 + 30H_2O$, which is soluble in alcohol, being garnet-red; it is obtained by heating a mixture of As_2O_3 and 2NaHS, filtering, and treating with alcohol, the aqueous solution containing the monosulphoxy-salt, AsO_3SHNa_2, H_2O, and the red alcoholic layer the above complex salt.

ARSENIC TRIBROMIDE : $AsBr_3$, which is colourless, melts at 25° and boils at 220°, **ARSENIC DI-IODIDE,** As_2I_4, and **ARSENIC TRI-IODIDE,** AsI_3, a red solid, are also known, and are formed from the elements in presence of carbon disulphide; they are decomposed by water. Numerous fluorides and selenides of arsenic have also been studied.

OXYGEN COMPOUNDS OF ARSENIC

Arsenic trioxide, arsenious anhydride, $As_4O_6(As_2O_3)$.
Arsenic pentoxide, arsenic anhydride, As_2O_5.
Arsenious acid, H_3AsO_3 (not known in the free state).
Arsenic acid, H_3AsO_4.

ARSENIC TRIOXIDE, ARSENIOUS OXIDE : As_4O_6, or As_2O_3

This compound is commonly called *arsenic, white arsenic,* or *arsenious acid.* It is found in small quantities in nature as *arsenolite,* As_2O_3, in octahedral crystals and in various minerals. It is formed by burning arsenic, or arsenic minerals in general, in presence of air; the As_2O_3, which is volatilised, is collected in suitable chambers. It is also formed as a white powder by oxidising arsenic with dilute HNO_3. It is ordinarily manufactured in large quantities from the dust which separates from pyrites gases (*see* p. 293), or from other arsenical minerals when they are roasted in a furnace.

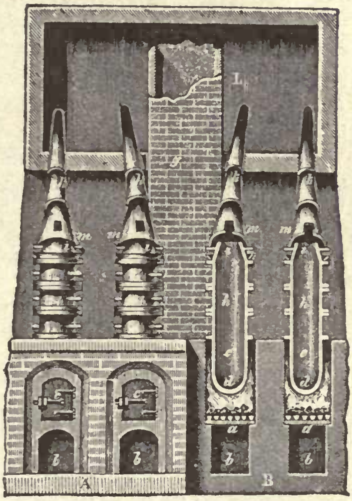


Fig. 167.

When arsenical pyrites, AsFeS, is roasted, arsenic sulphide is formed at a red heat, whilst at a white heat arsenious anhydride sublimes and SO_2 is driven off; the residue consists of oxide, sulphate, and arsenate of iron. If a direct-flame furnace is used, the resulting product is contaminated by the coal-dust, which partially reduces the arsenic oxide to arsenic and thus gives a grey colour. Muffle furnaces give purer products, but use more fuel. Producer gas does not contaminate the product, and is cheaper to use than a muffle furnace. The arsenious anhydride which sublimes is condensed as a white powder in chambers or in long zigzag channels, lined with lead; the gas afterwards passes through filters and escapes into the air with less than 0·15 grm. of arsenic per cu. metre. When the mineral on the hearth no longer flames, the roasting is at an end. Furnaces which treat 10 tons of mineral per 24 hours consume about 150 kilos of coal per ton, and the roasted residues contain less than 2·5 per cent. of arsenic. The crude arsenic flour thus obtained is purified by sublimation from iron retorts and then on slow cooling forms an amorphous transparent glass-like mass (vitreous arsenic) of sp. gr. 3·74, which gradually becomes opaque like porcelain. If, on the other hand, the vapour is rapidly cooled it is obtained in a crystalline form. The crystals are of the regular system and of sp. gr. 3·69; in nature it is sometimes found in a monoclinic form known as *claudetite,* As_2O_3. Arsenious anhydride may be obtained in the vitreous state also by compressing the flour at 150° under a pressure of 2500 atmcs.

In some works the sublimation is carried out in vertical, cast-iron, cylindrical retorts, holding 200 kilos of the material (Fig. 167), and surmounted by two or three cast-iron cylinders, *h*, of which the uppermost contains an opening, *m*, in order to facilitate the removal of any obstructions in the bonnet-shaped tubes by which it is surmounted, and which enter a condensing chamber, *L*. The whole is heated by direct flame, the temperature being gradually raised and finally maintained constant for twelve days, and the chamber, *L*, is kept at such a temperature that the As_2O_3, which condenses as a powder, is softened, and forms a compact mass, which, after being removed from the furnace and cooled, forms solid glassy blocks, suitable for sale. In the Figure the chimney, *g*, which causes the necessary draught is also shown. Regular blocks of vitreous or marbled white arsenic are obtained by compressing the powder in moulds and then heating the blocks so obtained more or less strongly and continuously. The workmen in arsenic works should wear overalls and a hood to cover the head, and their hands should be encased in gloves. They should also wash themselves with water containing a little ferric hydroxide (Bunsen's antidote).

A large part of the American arsenic trioxide is obtained at Ontario from the residues left after treating gold ores.

PROPERTIES. When heated in the air it sublimes at 218° without melting. Amorphous arsenic trioxide dissolves in 25 parts of water, the crystalline form requiring 80 parts of water; the solution has an acid reaction. It is easily soluble in HCl, but insoluble in alcohol: it has a sweetish taste, and is odourless and very poisonous.[1]

In spite of its highly poisonous properties this compound is used as a stimulant for ill-nourished people and for rapidly fattening beasts for market.[2]

It crystallises from hydrochloric acid in fine crystals, and during crystallisation the vitreous oxide becomes phosphorescent, whilst that which is opaque like porcelain does not show this phenomenon. When vapours of As_2O_3 are cooled rapidly, crystals of the regular system are obtained; but with slow cooling monoclinic crystals are formed. Acids dissolve arsenious oxide, and on boiling the solution in hydrochloric acid arsenic trichloride, $AsCl_3$, is volatilised; with nascent hydrogen it forms arsenic hydride, AsH_3. When it is heated with carbon an odour of garlic is produced, and it is reduced to free arsenic, which collects as a metallic mirror if the heating takes place in a closed tube. With strong oxidising agents, such as Cl or HNO_3, it forms arsenic acid.

The size of the molecule varies with the temperature; vapours at 500° to 700° contain a double molecule, As_4O_6; above 700° dissociation commences, and at 1800° only molecules of As_2O_3 are present.

Its heat of formation is 647 Kj. (154·7 Cals.), and its specific heat 0·1276.

USES AND STATISTICS. As_2O_3 is used in the preparation of numerous arsenical compounds, for the manufacture of certain pigments such as Schweinfurt green or Paris green,[3] for the preservation of hides, for treating

---

[1] According to J. B. Ekeley (1913), the arsenic in the body of a poisoned person is found mostly on the walls of the stomach and in the kidneys, then in the liver, on the intestinal walls, and in the heart; very little is found in the brain and in the spinal medulla, while a little is absorbed by the muscular tissues.

[2] White arsenic is administered, in gradually increasing doses, to oxen and horses to make them fatten more easily and render the skin shiny; when they perspire, such horses exude a dense white foam, which is highly valued in pure-bred horses. Animals may be accustomed to large doses of arsenic without exhibiting symptoms of poisoning; thus, sheep may be given as much as 15 grms. per day. Before these beasts are killed, the treatment with arsenic must be discontinued for at least fifteen days.

Some men (the arsenic-eaters of Lower Austria and Hungary) are able to tolerate doses of 0·25 grm. per day, which they take to make them healthy and robust and to prevent disease; under the influence of arsenic they are able to produce more physical labour, but when the treatment with arsenic ceases the organism rapidly degenerates.

[3] **Schweinfurt green** is a double arsenite and acetate of copper, $3Cu(AsO_2)_2 + Cu(C_2H_3O_2)_2$, and is obtained by treating, in a vat, 20 kilos of pure sodium carbonate with 25 litres of water at 80°, and then adding 39 kilos of powdered arsenious anhydride and stirring until solution occurs. The mass is next allowed to settle a little, the clear, hot solution being immediately drawn off into a lower vessel and treated with an almost boiling solution of copper sulphate. The precipitated copper arsenite is kept gently stirred to facilitate the evolution of CO_2, and after a rest acetic acid (46 kilos at 6° Bé.) and hot water are added. The mass is stirred and, when evolution of CO_2 ceases, the precipitate is allowed to settle, its dirty-green colour changing to a pure bright green. The solid mass is washed with hot water, filtered off, pressed, cut into cakes, dried at 35°, and finely ground. It forms a fine, emerald-green pigment, insoluble in water, but soluble in ammonia and in concentrated acids. The mother-liquors, treated with lime or soda, give greens of lower quality.

It is used as an oil- and water-colour, and is highly stable to air and light, but is turned brown by sulphurous gases. It was used for colouring wallpaper, toys, and even candles, but its use is now prohibited in most civilised countries, owing to its poisonous properties. It costs about £80 per ton.

felt in hat manufacture, as a mordant in calico printing, in the production of glass, in agriculture for fattening beasts, and for destroying rats and insects. At one time it was much used in aniline dyestuff factories, and now serves for the preparation of various medicines (*e.g.*, salvarsan or 606), and also for the treatment of chlorosis and epilepsy and for cauterising the nerves of the teeth. Sodium arsenite solutions are used in South America and South Africa to combat locusts and also mange in domestic animals.

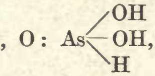
Commercial As_2O_3 in lumps costs about £28 per ton and in powder £24; the pure powdered product, for pharmaceutical purposes, is twice as expensive.

The world's production was 6000 tons of the value £94,000 (mean price, £16 per ton) in 1903 and 20,000 tons in 1910.

The output in tons for different countries is as follows. United States: 600 in 1903, 916 in 1907, 1325 in 1910, 2850 in 1912, and 2100 in 1913; the importation was 4000 tons in 1910 and 2700 tons (£32,000) in 1911. England: 917 tons in 1903, 1625 in 1906, 2880 in 1909, and 2153 (£17,600) in 1910. Spain: 1114 tons; and Portugal: 1320 tons in 1906. Germany: 2768 tons in 1903, 3000 tons in 1907, and 5000 tons in 1910. Canada: 233 tons in 1903 and 317 in 1906.

ARSENIOUS ACID: H_3AsO_3 or $As(OH)_3$.

This acid is not known in the free state; it perhaps exists in aqueous solution, although it appears to be dissociated into ions corresponding with the formula, H_3AsO_3, and more still with $HAsO_2$. Being a *tribasic* acid it is able to form three series of salts called *arsenites*. It ordinarily forms tertiary salts, for example, Ag_3AsO_3, which is of a yellow colour, and is obtained from the neutral solution of an arsenite with silver nitrate. The alkali arsenites are soluble in water and act as strong reducing agents, being transformed into arsenites, especially in presence of iodine. With silver nitrate in neutral solution yellow silver arsenite is formed which is soluble in acids and in ammonia. With H_2S in acid solution yellow As_2S_3 is precipitated, which is insoluble in acids but soluble in ammonium carbonate or sulphide.

The alkali salts appear to have an asymmetric constitution derived from the hypothetical dibasic acid,  $\mathrm{O:As}\!\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{H}\end{array}\right.$, corresponding with phosphorous acid.

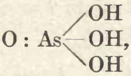
The arsenites of the other metals correspond with the formula, $H_6As_2O_6$, and are only slightly soluble or entirely insoluble in water. In cases of arsenic poisoning ferric hydroxide is administered as an antidote, as it forms an insoluble iron salt.

ARSENIC PENTOXIDE: As_2O_5 (ARSENIC ANHYDRIDE, ARSENIC OXIDE)

This compound is formed by heating arsenic acid, H_3AsO_4, until no further water is lost: $2AsO_4H_3 = 3H_2O + As_2O_5$, and forms a white glassy mass of sp. gr. 3·73, slowly soluble in water with generation of arsenic acid. On heating it strongly to redness it gives off oxygen and forms As_2O_3, and this explains why on burning As in the air As_2O_3 alone is formed, this being the more stable compound. Its true molecular weight has not yet been directly determined.

ARSENIC ACID: H_3AsO_4

This compound is formed by oxidising arsenic and As_2O_3 with concentrated nitric acid, and crystallises from the solution in rhombic prisms, $AsO_4H_3 + \frac{1}{2}H_2O$. At 100° it loses the water of crystallisation, forming H_3AsO_4, which is transformed at 140° to 180° into *pyroarsenic acid*, which forms white shining crystals: $2AsO_4H_3 = H_2O + As_2O_7H_4$. Pyroarsenic acid in turn loses water at 200°, forming white crystals of *meta-arsenic acid*, $HAsO_3$. These two latter acids regenerate arsenic acid with water. On heating a solution of arsenic acid in HCl, a portion of the former is volatilised as $AsCl_3$.

Ordinary or orthoarsenic acid is tribasic:  $\mathrm{O:As}\!\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.$, and forms three series of salts called *arsenates*, which are analogous to the phosphates and isomorphous with these. With silver nitrate in neutral solution it forms a *reddish-brown* trisilver arsenate, insoluble and analogous to silver phosphate, which is yellow, whilst arsenites in neutral solution, on the other hand, form a *yellow* precipitate. Hydrogen sulphide acts on acid solutions of arsenates forming a yellow precipitate of arsenic sulphide, insoluble in acid and soluble in ammonium sulphide or carbonate. With a mixture of NH_3, NH_4Cl, and magnesium sulphate (magnesia mixture) arsenates form a white crystalline precipitate of ammonium magnesium arsenate,

$$Mg(NH_4)AsO_4 + 6H_2O.$$

They also form a yellow precipitate, analogous to that produced by phosphates, when boiled with ammonium molybdate in presence of HNO_3.

Arsenic acid was at one time very much used in the manufacture of aniline dyestuffs. It is placed on the market to-day in strong solutions of 75° Bé. for use in calico printing at £36 per ton, or as a solid at £64.

ANTIMONY (STIBIUM): Sb, 120.2

This element occurs in nature more especially as the sulphide, Sb_2S_3, in *antimonite* or *stibnite* and less abundantly as oxide (*valentinite, cervantite, senarmontite*), while it accompanies arsenic in various minerals.

Antimony minerals are found particularly in Hungary, Bohemia, Germany, France, Corsica, Portugal, United States, Canada, Australia, Mexico, Turkey, India, Japan, etc. In Italy the principal mines are in Sardinia, Tuscany, and Sicily. The most important production of antimony minerals is now in the province of Hunan, China.

PROPERTIES. It is of more metallic appearance than arsenic, but, although it has some of the properties of the metals (lustre, electrical and thermal conductivity), in its chemical behaviour it is closely connected with arsenic and phosphorus. Five modifications are known: (1) the ordinary rhombohedral form; (2) black antimony; (3) yellow antimony; (4) explosive antimony; and (5) colloidal antimony. Only the first of these is of industrial importance.

Antimony has a silvery lustre and forms crystalline aggregates of the same form as those of arsenic: it is friable and has the sp. gr. 6·715. It gives an opaque grey powder, which becomes lustrous on compression.

Pure antimony which has been cooled slowly exhibits a shiny, lamellar fracture, whereas with a product which is impure or has been cooled rapidly, the fracture is granular and less lustrous. It melts at 629° and boils at 1440° (or at 229° in the cathodic vacuum).

Its specific heat is 0·0509, the coefficient of cubical expansion 0·000033 and that of linear expansion 0·0000115; the electrical conductivity at 18·7° is 4·29 (that of silver is 100 at 0°). It does not oxidise in the air, but when heated burns with a greenish-blue flame and emission of white vapours of the trioxide. It ignites in a stream of chlorine, is insoluble in HCl, and gives antimonious acid with dilute, and antimonic acid with concentrated, nitric acid. Unlike arsenic, it gives no odour of garlic when thrown on to glowing carbon.

INDUSTRIAL PREPARATION OF ANTIMONY. The antimony sulphide is first separated from the gangue in the crushed ore by heating the latter to redness in earthenware vessels or tubes[1] or over a direct flame in a furnace with a sloping floor, which conducts the fused sulphide (by liquation, *see* Part III) into a channel leading to a vessel outside, where it solidifies slowly.

---

[1] The clay crucibles each hold 10 to 25 kilos of the ore and have perforated bases; they are heated by direct flame in a furnace, where they are supported on channels into which the blue fused sulphide flows, passing out into large collecting crucibles immersed in sand to ensure very slow solidification. If the sulphide flowing out is red instead of blue, the temperature used is too high. The cost of liquation is about 24*s.* per ton of antimony sulphide.

If the temperature in the furnace is too high, some of the antimony sulphide vaporises and is lost, especially when direct flame is used. If the ore treated is too finely powdered, too much of the antimony sulphide remains in the residue.[1]

The sulphide is then broken up and heated in another furnace over a direct flame at a maximum temperature of 350°, being continually mixed until it is transformed completely, without fusion, into the oxide, which is only slightly volatile: $Sb_2S_3 + 10O = Sb_2O_4 + 3SO_2$; the temperature is raised somewhat at the end. The roasted mass is mixed with sodium carbonate (or sulphate), a little recovered slag and carbon, and the whole heated in crucibles. The fused antimony separates and, on slow solidification, is transformed into a characteristic, striated, crystalline mass:

$$Sb_2O_4 + 4C = 4CO + Sb_2.$$

Ores containing more than 90 per cent. of Sb_2S_3 are treated directly with carbon and sodium carbonate.

From sufficiently pure sulphides, antimony may also be obtained by heating it with iron in a graphite crucible, the following mixture being used: 65 per cent. of antimony sulphide, 27 per cent. of spongy iron (or tinned sheet scrap), 6 per cent. of calcined sodium sulphate, and 2 per cent. of carbon:

$$3Fe + Sb_2S_3 = 3FeS + Sb_2.$$

At a comparatively low temperature the iron removes all the sulphur from the antimony, and the ferrous sulphide forms with sodium sulphide a slag readily separable from the antimony regulus. The mass is discharged into an iron pan in which separation of the slag is completed, the iron still retained being removed by re-fusion of the antimony in the crucible in presence of a little pure antimony sulphide.

The most economical process is the English, in which the crushed antimony ore is charged, while still hot, into a furnace containing molten iron and iron sulphide; the antimony separates rapidly and may then be refined.

The English process has replaced almost all other processes, as it is more rapid and involves less loss. In the French process, the ore is roasted and the oxide then reduced with carbon in a reverberatory furnace fitted with a basic lining and communicating with a dust chamber to diminish the loss. The cost of obtaining a ton of antimony from a 50 per cent. ore is about £8.[2]

The refining of crude antimony is not always easy, since 0·1–0·3 per cent. S, 0·1–1 per cent. As, 0·2–0·6 per cent. Fe, 0·03–0·5 per cent. Cu, 0·3–0·7 per cent. Pb, etc., are present. The copper and lead are eliminated by fusing the crude product with pure antimony sulphide or with antimony oxysulphide (antimony blende, Sb_2S_2O); the arsenic and sulphur are removed by fusion with sodium carbonate; the lead is separated with greater difficulty by fusion in a furnace or in crucibles, first with sodium carbonate and, after removal of the slag, with antimony blende (prepared by heating a mixture of Sb_2O_3 and Sb_2S_3) and sodium carbonate or Glauber's salt. Since the slags separating during the refining contain much antimony, they are used in the treatment of antimony minerals (*see above*). The antimony solidifying under the slag exhibits stellate or fern-leaf striations, which are not formed with the impure metal. Refined antimony still contains about 1·5 per cent. of the above impurities.

---

[1] The percentage composition of a normal liquation residue, which may be subsequently treated together with poor ores for the direct extraction of metallic antimony, is: Sb_2S_3, 20·4; FeS, 2·87; FeS_2, 1·23; SiO_2, 59·84; Al_2O_3, 4·65; CaO, 5·22; CO_2, 4·10; alkali and carbon, 1·69.

[2] Certain Italian, Australian, French, and Hungarian ores contain, besides 40 to 70 per cent. of antimony as sulphide, also a little gold and silver, but their value is calculated without reference to these metals, and they may be satisfactorily treated by the English process. Ores containing noble metals and but little antimony are worked preferably by the French process.

The electrolytic industrial preparation of antimony has been attempted by the general process of Borchers and Siemens and Halske (Ger. Pat. 67,973, 1892), modified by Engelhardt and Nettel (U.S. Pat. 568,843, 1896), use being made of double salts obtained by dissolving antimony sulphide in alkali hydrosulphides: 30 per cent. of antimony sulphide (Sb_2S_3), 66 per cent. of $Na_2S, 9H_2O$, and 3 per cent. of sodium chloride. The process was improved in 1902 by Izart and Thomas and applied at the Cassagrac mines in France; diaphragms are used and caustic soda is introduced into the anodic chamber to prevent accumulation of sulphur and consequent formation of polysulphides, which would redissolve the antimony already precipitated. The current density used is 0·8 amp. per sq. dm. and the voltage 0·8, the current yield being 76 per cent. and the amount of antimony obtained per kilowatt-hour 621 grms. E. Ronco (1898) uses a sodium sulphantimonate solution (12° Bé.) and 3 per cent. of NaCl in iron vessels. A. G. Betts electrolyses a solution of antimony chloride (prepared from antimony sulphide and ferric chloride: $6FeCl_3 + Sb_2S_3 = 6FeCl_2 + 3S + 2SbCl_3$), anodes of lead or antimony being employed. Electrolytic processes are, however, not yet widely used.

APPLICATIONS AND PRODUCTION. This element has now acquired importance because it is an essential component of many metallic alloys which are largely used, for example, hard lead and *type metal*, which contains 25 per cent. of Sb, 10 to 20 per cent. of tin, a little copper, nickel, bismuth, and the remainder of lead. Of similar composition are stereotype plates.

Hard lead is used in many chemical industries, especially for cocks, and consists of lead containing 10 to 15 per cent. of antimony.

When mixed with tin it forms *Britannia metal*. When alloyed with zinc, copper, etc., it forms *white metal* (*anti-friction metal*), which is much used for bearings in place of the dearer alloys containing much tin. With tin and lead it forms various other alloys, especially pewters, which were formerly so largely used for kitchen utensils, dish-covers, mugs, etc.[1]

Several antimony compounds are used in considerable quantities to prepare the so-called antimony colours, such as antimony cinnabar (antimony oxysulphide), Naples yellow (basic lead antimonate), and antimony oxide, which forms a good substitute for zinc oxide, since it is more stable towards light and is not poisonous.

The product known commercially as " antimonium crudum " is not really crude antimony, but the sulphide (Sb_2S_3), and is used more especially for fireworks, while the pentasulphide, Sb_2S_5, serves for vulcanising and colouring rubber. Tartar emetic (potassium antimonyl tartrate) is largely used as a mordant in dyeing cotton with basic dyestuffs.

Commercial crude antimony often contains 1–3 per cent. FeS, 0·5–3 per cent. As_2S_3, 2–4 per cent. Pb, 0·1–0·6 per cent. Cu, and 1–3 per cent. Fe.

STATISTICS. The world's production of antimony in 1912 was about 24,000 tons, obtained from about 80,000 tons of ore.

In the *United States* the production of antimony was about 2628 tons in 1907, and fell later owing to the lowered price; in 1916 1800 tons were obtained from antimoniferous lead from native ores and 600 tons from imported minerals. In the same year 2600 tons of antimony were recovered from scrap alloy and converted into antimony alloys. The importation of pure metal was 4300 tons in 1909 and 3500 tons (£100,000) in 1910; that of antimony ore was 1700 tons in 1909 and 650 tons in 1910, besides 460 tons of antimony oxide or salts in 1909 and 160 tons in 1910. The United States imported also 6000 tons of type (£92,000) in 1910.

---

[1] The percentage compositions of various pewters are as follows: common pewter, 90 Sn, 9 Sb, 1 Cu; English pewter, 88·5 Sn, 7 Sb, 3·5 Cu, 1 Bi; pewter for dish-covers, 68·7 Sn, 17 Sb, 10 Zn, 4·3 Cu; so-called Queen's metal, 70–75 Sn, 8–16 Sb, 8–16 Pb, 8–16 Bi.

In *Germany* the production in 1905 was 2794 tons, and the importation in 1908 amounted to 2670 tons (2496 in 1907) of crude antimony, besides 1687 tons (3597 in 1907) of antimony ore, two-thirds of the latter from China and one-third from France; of the imported antimony, 28 per cent. came from France, 7 per cent. from Belgium, 11 per cent. from Austria-Hungary, and 54 per cent. from England. The production rose to 4970 tons in 1910 and 5411 tons in 1911. Germany exported 149 tons in 1908 (255 in 1907).

France produced 1786 tons of antimony in 1901, 2396 tons in 1905, and 4640 tons in 1910, and exported 1808 tons in 1913, 1600 in 1914, and 985 in 1915; 5258 tons of antimony ore were imported in 1913, 5180 tons in 1914, and 2826 tons in 1915 (in 1913 608 tons were exported). *Austria* produced 207 tons in 1907 and 162 in 1908; *Hungary*, 954 tons in 1906 and 600 in 1911; *Japan*, 206 tons in 1906 and 120 in 1910. *China* has a very large output—4000 tons in 1913 and about 8000 in 1914—but this is almost all in the hands of Japanese merchants and speculators.

In *Italy* the output of antimony and its ores has shown great variations; thus in 1907 7892 tons of ore (4404 in Tuscany, 3318 in Sardinia, and 170 in Sicily) were produced, 2841 in 1908, 2441 (£3266) in 1911, and 1878 (£4490) in 1912, 1822 tons with a mean content of 25 per cent. Sb in 1913; in 1914 the output of only 555 tons was obtained from two Sardinian mines, all the others being closed owing to the lowering of price; in 1915 4334 tons and in 1916 6509 tons were produced. The production of metallic antimony in Italy amounted to 1720 tons in 1901, 836 in 1904, 345 in 1908, 60 in 1909, and 138 in 1914. The quantity imported was 153 tons in 1908, 342 in 1910, 635 in 1912, 198 in 1914, 825 in 1915, and 156 in 1916. The amount exported from Italy is insignificant: 10 tons in 1908, 7·5 in 1910, 11 in 1912, 51 in 1914, 3·2 in 1915, and 188 in 1916. Formerly a large proportion of the antimony ore produced in Italy went abroad.

The *price* of antimony (and also that of the ore, to some extent) has undergone extraordinary variations during the last ten years. The unforeseen increases were due partly to the increased use of the metal in various alloys, but mainly to speculation; the latter has not always been successful, owing to miscalculation of the productive capacity of China, to the fact that in many alloys the antimony may be partially or totally replaced by other metals, and to occasional flooding of the market by accumulated stocks.

In 1901 antimony regulus was quoted at £30 per ton; in 1904 at £32, in 1905 at £50, in 1906 at £104, in 1907 at £70, in 1910 at £34, and in 1912 at prices varying from £30 to £44. At the beginning of 1914 the price was about £24 (London and Hamburg), and at the end of 1914, after the outbreak of the European War, it rose rapidly in Germany to £100–£120, and in 1915 and 1916 to fantastic amounts. In Italy between 1912 and 1914 the price fluctuated between £28 and £31 per ton, but at the close of 1914 it was £54, and in July 1917 more than £170 per ton.

EXPLOSIVE ANTIMONY. If a solution of antimony trichloride (at least 10 per cent.) is electrolysed with one antimony and one platinum electrode, a shining metallic coating is formed on the latter which explodes violently when rubbed with another substance. Gore, who first studied this in 1858, found that it was formed of 93·5 per cent. of antimony, 0·5 per cent. of HCl, and 6 per cent. of $SbCl_3$, and that the last substance could not be extracted with ordinary solvents; Cohen (1903) has therefore pointed out that electrolytic antimony cannot be used for atomic weight determinations. The cause of this special property of antimony is not at present known.

HYDROGEN ANTIMONIDE : SbH_3

This is perfectly analogous in all its physical and chemical properties to hydrogen arsenide, and, like the latter, but at a lower temperature, gives a black stain when heated, this being less shining than that of arsenic and insoluble in sodium hypochlorite solution.

With silver nitrate, SbH_3 gives black silver antimonide, $SbAg_3$, mixed with metallic silver.

The compositions of the hydrogen compounds of As and Sb are determined as with PH_3, by passing them over copper heated to redness.

ANTIMONY TRICHLORIDE : $SbCl_3$. This is easily formed by dissolving oxide or sulphide of antimony in concentrated hydrochloric acid : $Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3$; the solution is evaporated and the $SbCl_3$ then distilled.

It may also be prepared by treating the natural sulphide with an inadequate quantity of HCl, so as to obtain a product free from arsenic. Thus, 100 parts of the sulphide may be heated gently with 500 parts of commercial hydrochloric acid until dissolution and evolution of H_2S are almost complete, a little sulphur and gangue separating; after filtration through glass wool or asbestos and evaporation on a water-bath, the dense liquid remaining is distilled with a little powdered antimony : HCl first passes over, the temperature then rising to 223°, at which colourless antimony trichloride distils, this afterwards crystallising.

When pure it forms a colourless, corrosive, scaly, crystalline mass, melting at 73° and boiling at 223°. It is soluble in alcohol, acetone or carbon disulphide, and in the air absorbs moisture and becomes buttery (butter of antimony).

Butter of antimony is also obtainable directly from the concentrated hydrochloric acid solution of antimony sulphide (*see above*), by diluting it with dilute hydrochloric acid so as to obtain a mass of density 1·34–1·36 (33 per cent. $SbCl_3$); when mixed with 10 per cent. of olive oil it serves to give a brown surface to arms and iron articles.

Antimony chloride dissolves in water acidified with HCl, but dilution of the solution with 30 volumes of water causes the separation of a white powder (*powder of Algaroth*), consisting of a mixture of SbOCl (the oxychloride) and Sb_2O_3, and formerly used as a purgative and as an inferior white pigment; nowadays it is used especially for the preparation of the various antimony derivatives in a pure state.

ANTIMONY PENTACHLORIDE : $SbCl_5$. This is obtained by the very vigorous reaction caused by passing excess of chlorine over finely divided antimony, or more regularly by passing the calculated quantity of dry chlorine (15·5 grms.) into fused antimony trichloride (50 grms.).

It consists of a colourless or faintly yellow, very hygroscopic liquid which solidifies at a very low temperature and melts again at − 6°. It boils in a vacuum at 68° (14 mm.) and at the ordinary pressure it decomposes at 140° into $SbCl_3 + Cl_2$, and is consequently used for the chlorination of organic compounds.

With much water it decomposes into pyroantimonic acid ($H_4Sb_2O_7$) and HCl. With little water it yields the crystalline hydrates, $SbCl_5$, H_2O and $SbCl_5$, $4H_2O$.

Bromine, iodine, and fluorine derivatives are also known, these being analogou chemically to the chlorides.

ANTIMONIOUS FLUORIDE : SbF_3, obtained by dissolving Sb_2O_3 in HF, is of industrial importance because when mixed with sodium fluoride, NaF, it forms so-called *antimony salt,* which is used as a mordant in cotton-dyeing instead of tartar emetic, which costs more than double the amount with the same content of Sb_2O_3. Antimony salt, containing 47 per cent. of Sb_2O_3, costs about £40 per ton.

OXYGEN COMPOUNDS OF ANTIMONY

The lower oxide (Sb_2O_3) possesses no acid characters, even when dissolved in water, but is somewhat basic, and forms salts both with acids and with bases, showing that antimony has a somewhat pronounced metallic character. The pentoxide still possesses acid characters and thus forms antimonic acid, which behaves in an analogous manner to phosphoric acid, so that the classification of antimony with the non-metals is justified.

ANTIMONY TRIOXIDE (ANTIMONIOUS OXIDE): Sb_2O_3 or preferably Sb_4O_6

This compound is found in nature as *senarmontite*, in regular octahedra of sp. gr. 5·3, and as *flowers of antimony* in rhombic prisms of sp. gr. 5·57. It is not isodimorphous with As_2O_3, as was once believed; antimony is trivalent in it. It is prepared by burning antimony with a limited quantity of air or with steam or by oxidising it with dilute HNO_3. It is volatile at very high temperatures, and its vapour density at 1560° corresponds with the formula Sb_4O_6. At still higher temperatures simple molecules of Sb_2O_3 are probably also formed. It forms a yellowish-white crystalline powder, consisting of both regular and rhombic crystals. It is insoluble in water, HNO_3, and H_2SO_4, but is soluble in HCl, tartaric acid, and alkalis.

This oxide is used as a substitute for white lead, as it covers well; it costs about £50 per ton. *France* exported the following quantities of the oxide, including salts and kermes mineral (*see later*): 1488 tons in 1913, 845 in 1914, and 222 in 1915.

When heated in the air, the trioxide yields the *tetroxide*, Sb_2O_4.

The **HYDROXIDE**, $Sb(OH)_3$, corresponding with the oxide, Sb_2O_3, is not analogous to arsenious acid, AsO_3H_3, and is obtained from tartar emetic with dilute sulphuric acid. It easily loses water, forming *antimonyl hydroxide* or *white meta-antimonious acid*, SbO·HO, which forms Sb_2O_3 on heating.

When either the oxide or the hydroxide, $Sb(OH)_3$, is dissolved in sodium hydroxide solution it forms unstable salts called meta-antimonites, which are decomposed by simple evaporation of their aqueous solutions.

Antimonious oxide, Sb_2O_3, or the corresponding hydroxide, $Sb(OH)_3$, and also the metahydroxide, SbO·OH, which is usually obtained by precipitating $SbCl_3$ with sodium carbonate, also form salts with acids (metallic character); for example, $SbO_3(NO_2)_3$ or $Sb(NO_3)_3$, antimony nitrate, and also the sulphate, $Sb_2(SO_4)_3$.

The SbO radical in the metahydroxide, SbO·OH, which is called *antimonyl*, may be considered as a stable group, which has much the same function as a monovalent metal, so that the compound is analogous to K·OH, and as such forms salts, $SbO{\cdot}NO_3$, antimonyl nitrate, and $(SbO)_2SO_4$, antimonyl sulphate. A more important salt is *tartar emetic*, the double tartrate of potassium and antimonyl, $K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$, which is obtained by boiling a solution of cream of tartar (potassium hydrogen tartrate) with Sb_2O_3.

These salts, especially the organic salts, are, however, decomposed on simple dilution with water, which shows that antimonious oxide has only a *weakly* basic character.

ANTIMONY PENTOXIDE (ANTIMONIC ANHYDRIDE): Sb_2O_5

This compound is formed on oxidising antimony with fuming nitric acid or on heating antimonic acid to 300°. It consists of a bright yellowish powder of sp. gr. 5·6, insoluble in water and in nitric acid. It is soluble, however, in concentrated HCl, and also in aqueous solutions of alkali sulphides. On fusion with alkali carbonates it forms *antimonates*. Antimony is pentavalent in it.

ANTIMONY TETROXIDE. Above 300° the pentoxide commences to decompose, forming oxygen and antimony tetroxide, Sb_2O_4, that is, $SbO_2{\cdot}O{\cdot}SbO$ (a mixed antimonious-antimonic anhydride), which forms a white powder becoming yellow on heating, does not melt and is not volatile, and decomposes at about 950° into oxygen and antimony trioxide, Sb_2O_3; as with arsenic, the oxide most stable at a high temperature is Sb_2O_3 or Sb_4O_6.

The tetroxide is formed also by oxidising antimony or its sulphide with excess of air It occurs more or less pure in nature as *valentinite* and *cervantite*.

ANTIMONIC ACID: H_3SbO_4. This compound may be obtained by heating antimony with concentrated nitric acid or by adding $SbCl_5$ to cold water:

$$SbCl_5 + 4H_2O = SbO_4H_3 + 5HCl.$$

It is obtained more conveniently by precipitating a solution of potassium antimonate with nitric acid; potassium metantimonate, $KSbO_3$, is obtained by melting 1 part of antimony with 4 parts of potassium nitrate, and with water this forms monopotassium antimonate, KH_2SbO_4, which in turn yields antimonic acid with nitric acid.

It forms a white powder ($2H_3SbO_4 + H_2O$), almost insoluble in water and in nitric acid, and has a weak acid reaction. It is a tribasic acid, but ordinarily behaves as though it were monobasic. At a temperature of 100° it loses water, forming *pyroantimonic acid*, $H_4Sb_2O_7$; at 175° it is transformed into *metantimonic acid*, $HSbO_3$, and at 275° this is then transformed into antimony pentoxide, Sb_2O_5.

PYROANTIMONIC ACID : $H_4Sb_2O_7$, is known more especially in the form of its salts, of which dipotassium pyrantimonate, $K_2H_2Sb_2O_7 + 6H_2O$, is used as a reagent for the precipitation and recognition of sodium compounds, because it forms with these a crystalline disodium pyrantimonate, $Na_2H_2Sb_2O_7 + 6H_2O$, which is insoluble in cold water.

SULPHUR COMPOUNDS OF ANTIMONY

ANTIMONY TRISULPHIDE : Sb_2S_3 (black sulphide of antimony). This is found in nature crystallised in dark grey, rhombic, radiating, lustrous masses of sp. gr. 4·7, the name *stibnite* being given to these. When obtained by liquation of the ore it is termed crude antimony (*see above*), and contains up to 97 per cent. of Sb_2S_3. When heated it melts and then distils (sublimes). When prepared by precipitation of a salt or oxide of antimony in acid solution by means of hydrogen sulphide, it forms a red, amorphous mass (which tenaciously retains 1 per cent. of H_2O), which, after being dried at 200° or treated with dilute HCl in the hot, is converted into a blackish, crystalline mass. In hot, concentrated HCl it dissolves, giving H_2S and $SbCl_3$.

The pure trisulphide is obtained by treating finely powdered crude antimony for a couple of days with double the quantity of 10 per cent. ammonia solution, the liquid being then decanted off and the fine, brownish-grey powder—which is used for pharmaceutical purposes, as it is free from arsenic—washed and dried.

It is used also in fireworks, for ruby glass, and in matches (*q.v.*); the sulphide obtained by the wet way serves also for vulcanising rubber, to which it imparts a reddish-brown colour.

The price of crude antimony (leaving about 1 per cent. of insoluble residue when boiled with 10 parts of hydrochloric acid) is usually one-half of that of antimony regulus (*see above*). The pure black sulphide costs normally about 1*s.* 7*d.* per kilo and the red sulphide about 5*s.* 6*d.* Stibnite containing 90 per cent. of Sb_2S_3, when ground fine, is used directly in oil pigments (grey).

CINNABAR OF ANTIMONY : $(Sb_2S_2O)_3$. This is found ready formed in nature, and is also prepared artificially by treating $SbCl_3$ with a solution of sodium thiosulphate, or better still by heating Sb_2S_3 in a current of air and steam. It is used as a red colouring matter to replace ordinary cinnabar, and costs from £48 to £160 per ton, according to the quality.

Kermes mineral, used in medicine, is a mixture of antimony trisulphide and antimony trioxide. It is obtained by boiling antimony sulphide with a solution of sodium carbonate.

ANTIMONY PENTASULPHIDE : Sb_2S_5. This substance is also called *golden antimony sulphide*. It is obtained from antimonic acid in weak acid solution and hydrogen sulphide, or by treating a solution of sodium thioantimonate, SbS_4Na_3, with dilute HCl or H_2SO_4, H_2S being formed simultaneously. It forms an orange-red powder, insoluble in dilute acids, whilst it dissolves in strong HCl, forming sulphur, H_2S and $SbCl_3$. When heated strongly it decomposes into black Sb_2S_3 and sulphur.

The pentasulphide or golden sulphide was formerly much employed in medicine and in veterinary surgery as a sudiferous expectorant. It is only used to-day to vulcanise rubber and to impart to it a red colour, and also in certain match factories. It costs from £60 to £140 per ton, according to its state of division, degree of colour, and free sulphur content.

SODIUM THIOANTIMONATE (Schlippe's salt), $Na_3SbS_4 + 9H_2O$, is obtained by fusing 50 parts of dry sodium carbonate with 30 of powdered sulphur, 8·5 of pure antimony trisulphide, and 6 of powdered wood charcoal; the fused mass is allowed to solidify in a thin layer, and is then powdered and dissolved in hot water and the solution filtered and allowed to crystallise by cooling. The salt crystallises in large, yellowish tetrahedra, and in the air rapidly becomes covered with a brown layer of Sb_2S_5, since it is decomposed even by carbonic acid; it is insoluble in alcohol, and is used in pharmacy to prepare the pure golden sulphide, the salt being dissolved in 8 parts of cold water and the solution treated gradually with dilute HCl.

Free *thioantimonic acid* is unknown.

Potassium thioantimonate, $K_3SbS_4 + 4\frac{1}{2}H_2O$, which is reddish-yellow, is the principal component of *liver of antimony*, and costs about 2*s*. per kilo.

GROUP OF VANADIUM, COLUMBIUM, AND TANTALUM

This group is connected with the phosphorus group, especially on account of the analogy which exists between the derivatives of the two groups, and also because the more highly oxidised compounds have an acid character. In the free state, however, they are similar to the metals, especially to chromium, iron, and tungsten. The three elements are very rare.

VANADIUM : V, 51.3. This element was discovered by Del Rio in 1801, who confounded it with chromium. In 1830 Sefström characterised it as an element. It is found in nature more especially in *vanadinite*, $PbCl_2, 3Pb_2(VO_4)_2$, which contains about 17 per cent. of vanadic acid; in *Mottramite* $(PbCu)_3(VO_4)_2$; in *Roscoelite* (a vanadium and aluminium silicate with 28·85 per cent. of vanadic acid); in *Descloizite* [lead and zinc vanadate, $(PbO, ZnO)_4, V_2O_5, H_2O$, with 22·46 per cent. of vanadic acid]; and in Peruvian vanadium sulphide (containing 39·84 per cent. of the sulphide). Vanadium ores are found mostly in Sweden, New Zealand, Peru, etc.

For some years now the vanadium mines in Colorado (at San Miguel and Montrose) have been of importance. A ton of ore with 3 per cent. of vanadium is worth about £12 (1912). For some time the basic slag of the Creusot works in France has been treated for the extraction of vanadic acid.

It is obtained in the metallic state by heating vanadium chloride in a current of hydrogen. A greyish powder is thus obtained of metallic lustre and of sp. gr. 5·5. It is difficult to melt and is oxidised only very slowly in the air. It is obtained in less pure silver-white crystals, containing 4 per cent. of carbon, by heating vanadic acid and carbon in an electric furnace in a current of hydrogen. Its specific gravity is then 5·8.

From oxygenated ores or from sulphides, sodium vanadate is obtained by torrefaction and subsequent fusion with soda; the fused mass is acidified with HCl, and the vanadate precipitated with a lead, barium, or iron salt.

These vanadates may be used directly for making vanadium alloys or vanadic anhydride. Treatment in the electric furnace of a mixture of ferric oxide, vanadic acid, silica, and coke yields a double iron-vanadium silicide (45·04 per cent. V, 33 per cent. Fe, and 20 per cent. Si), which, when added to steel, facilitates the escape of the included gas.

Almost pure vanadium is obtained by Goldschmidt's alumino-thermic process (*see* Part III: Thermit), by mixing V_2O_5 with calcium and aluminium in the ratio of 3 atoms of Ca and 2 of Al; the vanadium regulus, free from gas-bubbles, contains up to 94 per cent. V, while with the thermit process in magnesia crucibles, Vogel and Tammann obtained a 99 per cent. vanadium regulus. In practice it is convenient to prepare by the thermit process ferrovanadium with 25 per cent. V, which may be used directly in the preparation of special steels. As little as 0·15–0·25 per cent. of vanadium increases the hardness and tenacity of soft steel; as a rule, 2–3 per cent. of chromium is also added to these steels.

The electrolytic preparation of vanadium has also been tried, but without great success. G. Gin made a plastic mass of V_2O_3, retort carbon and tar, which was heated, ground, and compressed in the form of cylinders, these being united in bundles to serve as anodes, while steel blocks were used as cathodes; the electrolyte consisted of a fused mixture of calcium and vanadium fluorides (V_2F_6 and $3CaF_2$), the voltage was 10–15, and the current 2 amps. per sq. cm. of anode surface and 6 amps. per sq. cm. of cathode surface. If iron is added during the course of the electrolysis, ferro-vanadium is obtained directly, otherwise pure vanadium separates.

According to U.S. Pat. 1,065,582 (1913), pure vanadium is obtained by treating the sulphuric acid extract of the ore (carnotite, etc.) at 90° with the quantity of lead sulphate necessary to transform all the vanadium into lead vanadate [$(PbO)_3V_2O_5$], which is precipitated and collected pure on a filter and then transformed by means of sulphuric acid into pure vanadyl sulphate.

When heated, vanadium burns to V_2O_5; it also combines readily with nitrogen, giving the nitride, VN.

Derivatives analogous to those of phosphorus are well known, such as *vanadium trichloride*, VCl_3; *vanadium trioxide*, V_2O_3, which is obtained by heating V_2O_5 to redness in a current of hydrogen and forms a black powder. The corresponding *sulphate*, $V_2(SO_4)_3$, is also known, and forms alums with alkali sulphates in the same way as iron and chromium.

Vanadium pentoxide, V_2O_5, dissolves in alkalis, forming salts of *vanadic acid*, H_3VO_4, and of *metavanadic acid*, HVO_3.

The *vanadates* are isomorphous with the corresponding phosphates. *Ammonium metavanadate*, VO_3NH_4, is insoluble in solutions of ammonium chloride and serves to separate vanadium from its ores. These are first melted with sodium hydroxide and potassium nitrate in order to obtain sodium vanadate, which is soluble in water. On adding ammonium chloride to this solution NH_4VO_3 is precipitated and yields V_2O_5 on heating. *Vanadous oxide*, VO, a *dioxide*, VO_2, a *dichloride*, VCl_2, a *tetrachloride*, VCl_4, and an *oxychloride*, $VOCl_3$, are also known. *Vanadic salts* of the type VX_3, and *vanadous salts*, VX_2, are known. *Vanadous sulphate*, VSO_4, crystallises with $7H_2O$ and is isomorphous with various metallic sulphates.

USES. Certain vanadium compounds are used industrially, for example, in the dyeing and printing of cotton (aniline black), as vanadic acid readily gives up oxygen to reducing agents, which it oxidises, and thus acts as an oxidising catalyst. By the action of hydrogen peroxide on the oxides and acids of vanadium, variously coloured peroxides and peracids of vanadium are obtained. Vanadium salts are sometimes used in the manufacture of glass and porcelain. The principal use of metallic vanadium is in metallurgy, in the preparation of special steels of high value. For this purpose vanadium is placed on the market at £4 to £4 8*s.* per kilo. This is obtained in the electric furnace Pure vanadium costs more than £40 and vanadic acid more than £6 8*s.* per kilo.

COLUMBIUM: Cb, 93.5 (discovered by Rose in 1844) and **TANTALUM: Ta, 181.** These elements are found together in certain rare minerals, in the form of columbates and tantalates, for example, in *columbite*, [$(Fe, Mn)Cb_2O_6$], and *tantalites* ($FeTa_2O_6$). The chlorides, $CbCl_5$ and $TaCl_5$, are decomposed by water. This is also the case with the fluorides and the double fluorides, 2KF, CbF_5 and 2KF, TaF_5, which are used for the separation of the two elements, because the former is soluble and the latter insoluble in water. The oxides, Cb_2O_5 and Ta_2O_5, form with alkalis the salts of *columbic* and *tantalic* acids, CbO_4H_3 and TaO_4H_3. When columbic acid is heated with carbon in the electric furnace free columbium is obtained; this, like boron and silicon, is very resistant to the action of acids.

Tantalum nitride, TaN, is also known.

Tantalum has now acquired great importance, especially on account of its application in the manufacture of electric lamps with tantalum filaments, prepared by the firm of Siemens and Halske. These lamps consume less than half the electric energy of the ordinary incandescent lamps with a carbon filament, for the same intensity of light.

Tantalum is now prepared in the pure state by forming small rods of a paste of tantalum pentoxide and paraffin wax and then immersing these in powdered charcoal at a temperature of 1700°; brown tantalum tetroxide, a good conductor of the electric current, is thus formed; this is then placed in a glass vessel, which is evacuated and an electric current passed through it; oxygen is evolved and pure tantalum remains. On the large scale the double fluoride of potassium and tantalum, 2KF, TaF_5, is heated with metallic sodium and the metallic tantalum so obtained purified by melting it in the electric arc *in vacuo*, after first rendering it a conductor by means of high pressure.

Pure tantalum melts between 2250° and 2300°, and has a specific gravity of 16·6, a specific heat of 0·0365 from 10° to 100°, and a specific resistance of 0·165 for a length of 1 metre and a cross-section of 1 sq. mm. When tantalum is heated to redness and transformed into a sheet with a mallet, and then heated to redness and hammered repeatedly, it finally acquires a hardness equal to that of the diamond and a greater power of perforation; it is also remarkable for its high tenacity and its resistance to chemicals, especially acids; its extraordinary hardness is perhaps due to the presence of traces of oxide.

Since tantalum resists the action of acids, aqua regia and also alkaline solutions, it is now used instead of platinum for the preparation of electrodes and of vessels to resist acids, chlorine, and oxidising agents. For this purpose the manufacturers start from *tantalum hydride*, which is considered by some as a stable alloy of H and Ta. This is worked to a paste and the objects to be prepared are moulded to the desired shape and heated to 1200°, when the hydrogen escapes and compact and homogeneous tantalum remains without the necessity of heating to the melting-point of 2300°.

Tantalum lamps are produced in a similar manner to incandescent carbon lamps by means of a small glass bulb which is evacuated, and in the interior of which is half a metre of very fine tantalum filament (0·05 mm. in diameter) which is arranged in zigzag form, being supported on small hooks which hold it taut. These lamps, of 25 candle-power or more, are sold at about 1*s.* 6*d.*

CARBON GROUP: (C, Si, Ge, Sn)

This group comprises four elements, namely, two non-metals, carbon $C = 12$ and silicon $Si = 28{\cdot}3$, and two metals, germanium $Ge = 72{\cdot}5$ and tin $Sn = 119$.

All these elements are tetravalent and combine with the halogens, forming compounds of the general formula, MX_4, in which M is the tetravalent element of this group and X the monovalent halogen. They all combine with oxygen forming compounds of the general formula, MO_2, which possess an acid character. On the other hand, whilst carbon and silicon readily form volatile hydrogen compounds in common with all the other non-metals, germanium and tin are clearly distinguished by not forming such, and generally behave as metals. We shall, therefore, study them further in the portion of this volume devoted to metals.

CARBON: C, 12

This is one of the most widely diffused elements in nature and is the principal component of all organic compounds. It is also found abundantly in inorganic compounds, such as marble, dolomite, etc. In combination with hydrogen it forms petroleum, paraffin wax, etc. In combination with oxygen it forms carbon dioxide and carbon monoxide.

It is found naturally in the free state in three allotropic forms, namely, as diamond, which is crystalline and transparent, as graphite, and as amorphous carbon. None of these forms possesses much chemical activity under ordinary conditions, although carbon in a state of combination is able to give rise to thousands of compounds.

Carbon does not melt even at 3500°, and in the electric arc it is volatilised directly. The three allotropic forms of carbon all burn in oxygen, yielding carbon dioxide.

These allotropic forms differ from one another by containing varying quantities of internal energy, which may be determined indirectly by measuring the thermal tonality of their conversion into CO_2—by burning 12 grms. of each of the allotropic forms separately in oxygen. Thus the thermal tonality for amorphous carbon is 97,650 cals., for graphite 94,910, and for diamond 94,310; from which we may deduce that during the transformation of 12 grms. of amorphous carbon into graphite 2840 cals. are evolved, and that in passing from 12 grms. of graphite to the same quantity of diamond a further 500 cals. will be evolved.

DIAMOND. This substance is found more especially in South Africa, where diamonds of the total value of £140,000,000 have been extracted during the last forty years (at the Cape six new mines yielded diamonds to the amount of 34,000 carats in 1902 and 1903); in Brazil, from which about 2000 kilos of diamonds have been exported from 1727 up to date, and in India and Borneo. These diamonds are found mixed with siliceous sand and sedimentary rocks; diamond is also found in meteoric iron. In 1906 Brazil exported diamonds to the value of £1,000,000 and black diamonds (carbonado) to the value of £840,000.

Diamond is generally considered as the hardest of all known substances and forms the degree of 10 on Mohs' scale; crystallised boron is, however, equally hard. Diamond is therefore used for cutting glass and for the cutting surfaces of rock-drills; for this purpose coloured diamonds of small value are used.

It crystallises in the regular system, rarely in octahedra, more often in rhombodic decahedra. The crystalline faces are not perfectly plain, but are slightly convex. Diamond powder is of a dark grey colour and when very fine appears almost black.

If a diamond is colourless its high degree of transparency and refractivity constitutes its very high value. When, however, the colorations, which are due to certain impurities, are very beautiful, they may even increase its value rather than decrease it. When it is coloured black it has no great value, is called *carbonado*, and is employed for rock-drills. When thus crystallised its specific gravity is 3·5, and its index of refraction, *n*, is 2·42. At very high temperatures, between the two poles of a powerful electric battery, it softens, swells up, and then assumes a graphitic appearance. In an atmosphere of hydrogen free from oxygen diamond may be heated for hours at 1500° without undergoing alteration, whilst in a current of CO_2 it blackens, owing to the dissociation of the CO_2; at these high temperatures it changes if in contact with silica or silicates (CSi being formed), whereas it does not alter if in contact with sugar charcoal and does not soften even at 2300°. Unlike graphite it is not an electrical conductor.

In 1694 Averani and Targioni, of the Accademia del Cimento, succeeded in burning diamond. Lavoisier in 1775 and Davy in 1814 showed that on burning diamond in the air carbon dioxide alone was formed. In oxygen it burns at 700°, giving CO_2, although it is not attacked by a mixture of nitric acid and potassium chlorate.

Various hypotheses on the origin of diamonds have been put forward, but none of them has any positive basis. It is, however, probable, according to Moissan, that they are formed from carbon derived from the decomposition of organic matter at high temperatures and pressures in the interior of the earth. The carbon would thus be liquefied and would then crystallise during very slow cooling. It is also supposed that there may be large deposits of diamonds in the interior of the earth's crust. The other forms of carbon are obtained when diamond is heated to high temperatures without pressure and then evaporated without being liquefied, condensation in the graphitic form occurring in the colder parts of the vessel. Under the action of cathodic rays diamonds slowly turn brown.

In the Kimberley district the diamonds are usually found in an argillaceous layer of the "blue ground" at a depth of 15 to 20 metres. The diamondiferous earth extracted is broken up in rotating mills, the mud being washed away; treatment in centrifugal cylinders results in the accumulation of the diamonds present in the residue (about 1 per cent. of the earth treated). Further enrichment is effected in suitable pulsators, this being followed by passage over oscillating planes smeared with vaseline, which retains the diamonds; when the vaseline is melted in a boiler, the diamonds collect on the bottom. The tenacious retention of diamonds by vaseline and fats was discovered a few years ago.

Diamonds acquire a high value on being cut, that is, after facets have been formed, converting them into *brilliants* or into *rosettes*. Diamonds are cut by means of diamond dust. Diamonds of any value are weighed in conventional units.[1] At one time use was made of the *grain*, which was the constant weight of a dried Indian seed, but to-day the *carat* is in use and corresponds with *four grains*, or 205 milligrams. The value of a diamond is not proportional to its weight, but the value of each carat increases with increase of the total weight. The principal factor of the value is, however, the purity of the water and the refractive power towards light. Diamonds weighing one carat cost on the average £8; if they weigh two carats they cost £16 per carat; three carats £20 per carat; five carats £24 per carat; six carats about £26 per carat, etc.

In 1893 Moissan obtained *artificial diamonds* in very small scales up to 0·5 mm. long, and in 1905 he obtained some of 0·75 mm. diameter by saturating molten iron at a high temperature (1100° to 3000°) in the electric furnace with carbon and then cooling it rapidly. At such temperatures iron dissolves considerable quantities of carbon, which remain enclosed in the iron under very high pressure on cooling.[2]

---

[1] The most celebrated diamonds are the following:

The *Regent* or *Pitt* diamond weighs 136¼ carats. Its value has been estimated at more than £480,000, and it is the purest and finest stone known. It belonged to the Treasury of the French Crown and is to-day in the Museum of the Louvre in Paris.

The *Polar Star* weighs 40 carats, and belongs to the Crown treasures of Russia.

The *Orlow* weighs 195 carats and for a long time formed one of the eyes of a statue of Brahma. It was acquired in 1794 for £80,000, and was sold for an annuity of £640 yearly and a title of nobility for the vendor. It is to-day placed at the extremity of the sceptre of the Tsar of Russia.

Southern Star. When found in Brazil it weighed 250 carats, and after cutting in order to transform it into a brilliant its weight was 125 carats.

The *Florentine* weighs 139½ carats. It has a slight yellowish tint which is not apparent in artificial light, when it appears very brilliant. It now forms part of the Crown treasures of Austria. Its value is estimated at £100,000.

The *Great Mogul* now weighs 280 carats, whilst until the year 1600 it weighed 787 carats. Through the inexperience of some one who ordered it to be cut by an incapable person, it was greatly reduced in weight during cutting. It came originally from India and now belongs to the English Crown.

The *Koh-i-noor* weighed 280 carats before 1850, and was acquired in that year by the English Crown and cut in Amsterdam; to-day it weighs only 106 carats.

The *Sancy* weighs 53½ carats. It was bought by Antonio of Portugal in 1489. It then passed to the King of France, and was bought in 1835 by Prince Demidoff of Russia for £80,000 and resold in 1836 in Paris for £26,000.

The *Shah* weighs 86 carats and is very pure. It was presented to Alexander II of Russia by a Persian prince, and has been set in a chain to be carried round the neck.

The *Pasha of Egypt* weighs 40 carats. It is a blue diamond, the beautiful and intense colour of which is due to minimal traces of metallic oxides. It was sold in 1908 to the Sultan of Turkey for £80,000 in spite of its comparatively small weight.

The *Great Victoria* is a large diamond which was found at the Cape in 1884 and weighed 457 carats.

The *Excelsior* was found at Jagersfontein in the Orange Free State in June 1893, and was then the largest diamond known, having a weight of 972 carats. It is a very fine diamond of a slightly bluish shade and was valued at £1,000,000. Its first owner was Bernheimer, who then deposited it in the Bank of England.

A diamond weighing 3032 carats was discovered on January 26, 1905, at Pretoria in the Transvaal, and was supposed to have a value of £800,000. After it was cut by experts at Antwerp the finest piece formed the brilliant *Cullinan*, weighing 800 carats, which is valued at about £160,000. It was then acquired by the Cape Colony, which presented it to the King of England in 1909.

[2] In Italy Quirino Maiorana (1898) tried heating carbon by the voltaic arc in a steel chamber in which a very great pressure was suddenly developed by an explosive; microscopic diamonds were thus obtained. In 1909 the physicist Michele La Rosa pointed out that, although it may be true that carbon sublimes without melting at the temperature of the voltaic arc (3500° to 4000°) and that condensation of carbon vapour always yields graphite, yet it had not been demonstrated that carbon cannot melt at a higher (or even lower) temperature under the ordinary pressure. Thus, iodine has a marked vapour pressure even at the ordinary temperature and sublimes, but at 114° it melts and at 200° boils. La Rosa tried first to heat the purest sugar carbon in the singing arc (*see* p. 221) at the ordinary pressure, and he thought he had obtained the formation of small drops of liquid carbon; he attempted also the liquefaction of carbon in slender rods by passing through them very strong electric currents, and thus caused the rods to soften till they broke into rounded fragments resembling drops soldered together and having a graphitic character. In 1913,

Fused magnesium silicate also dissolves carbon, which then separates on cooling in the form of small scales of diamond. Burton (1907) found that an alloy of 100 parts of lead and one of calcium dissolves appreciable amounts of carbon at a lower temperature than iron does.

GRAPHITE (PLUMBAGO)

This occurs in nature crystallised in lamellæ or hexagonal plates, or in shining, amorphous masses readily cleaveable.

The oldest graphite mines are those of Borrowdale (Cumberland), and large quantities of graphite have been obtained from important mines at Irkutsk (since 1856); mines were afterwards discovered in Austria, which has now a greater output of graphite than any other European country. Important deposits of amorphous graphite are now utilised in the United States (Pennsylvania, Alabama, and Tigonderoga) and Mexico. Graphite is produced also in Canada, India, Japan and, since 1912, Madagascar. France produces graphite at Cradonet, Arriège, the Department of the Rhone, and Madagascar. In Italy impure graphite is found at Monte Pisano and Monte Amiata and also in Piedmont and Liguria. A little graphite is now obtained in Germany (at Passau). The most important mines in the world, for both quantity and quality of product, are those of Ceylon, where about 30,000 workpeople are employed and a duty of 8*s.* is paid for every ton of graphite exported.

It is greyish-black and leaves a persistent grey mark when rubbed on white paper; owing to this property it has been used since the sixteenth century for the preparation of pencils. Whereas almost all the graphite was formerly utilised for this purpose, only 4 per cent. of the present production is so used. Owing to the marked resistance of graphite to chemical reagents and high temperatures, much is now used for making crucibles in which metals are fused; in consequence of its high electrical conductivity, still more is used for the manufacture of the large electrodes for electric furnaces, now employed in large numbers in the production of calcium carbide, aluminium, cast-iron, steel, phosphorus, etc. A very large amount of graphite is now consumed in making carbons for arc lamps, and a large quantity of finely powdered graphite (plumbago) for preserving iron from rusting and granular black blasting or sporting powder from moisture.

The value of graphite in the preparation of crucibles—even when mixed with clay—lies in its low coefficient of expansion; thus the crucibles do not crack readily on rapid change of temperature. Oxidation of graphite is very slow up to 920°, but afterwards increases rapidly; a crucible composed of equal proportions of graphite and clay conducts heat far more rapidly than one of clay.

A crucible of refractory clay coated with a thin layer of graphite may be heated to 1815° without indication of fusion, whereas without such coating superficial fusion is much more easy. Graphite is soft (hardness 0·5–1 on Mohs' scale) and its specific gravity varies with the purity from 1·9 to 2·2. It differs from diamond by giving, when treated with concentrated nitric acid and dry potassium chlorate, yellowish crystallised graphitic acid (Brody's reaction), whereas amorphous carbon yields carbon dioxide; with concentrated sulphuric acid and potassium permanganate (or chromic acid) the reaction is more marked (Charpy, 1909). Potassium permanganate in alkaline solution oxidises it (and also amorphous carbon) to mellitic acid. It has a high thermal and electrical

---

Lummer completely liquefied carbon by heating it in the voltaic arc (220 volts) at reduced pressure: at 50 to 60 cm. of mercury it begins to boil, at 40 to 50 cm. it is viscous, and below 40 cm. quite liquid; the drops then assume an angular aspect (possibly diamond) and at 10 cm. boiling ceases and the mass is transformed into solid graphite. In 1907 (French Pat. 4566) Boismenu claimed that he obtained diamonds 2·5 mm. in diameter by electrolytic decomposition of fused calcium carbide by means of a continuous current: the calcium is liberated at the negative pole as a red vapour, and in this atmosphere the carbon cannot oxidise, and crystallises within the fused carbide in the zone of the positive electrode.

conductivity, which increases with its purity. The electrical conductivity increases with rise of temperature, as with conductors of the second class; it is used, therefore, for electric batteries and for dynamo brushes. Out of contact with the air it does not alter even at the highest temperatures (like diamond). When heated in oxygen it forms carbon dioxide, but with more difficulty than diamond; it leaves 2 to 5 per cent. of ash.

Its specific heat varies with the temperature, being 0·1138 at – 50°, 0·1990 at + 58°, and 0·4589 at 1000°.

When moistened with fuming nitric acid and then heated to redness, true graphites swell, forming a kind of Pharaoh's serpent; the name *graphitites* is given to those varieties which do not swell under these conditions (Luzi, 1891).

When treated with potassium chlorate and concentrated nitric acid true graphites are transformed slowly and completely into a crystallised yellow mass of graphitic oxide or acid, insoluble in water and nitric acid and formed of microscopic rhombic plates; it contains 56·3 per cent. C, 1·86 per cent. H, and 41·84 per cent. O, and decomposes violently when heated, forming a very light, flocculent black mass. Under similar treatment graphitites give a graphititic acid which contains 51·95 per cent. C, 1·80 per cent. H, and 46·25 per cent. O, and when heated yields a heavy, fine, black mass.

Graphites may be obtained artificially by passing a mixture of acetylene with carbon monoxide or dioxide through heated tubes or over heated calcium carbide: (*a*) $C_2H_2 + CO = 3C + H_2O$; (*b*) $2C_2H_2 + CO_2 = 2H_2O + 5C$; (*c*) $CaC_2 + CO = 3C + CaO$.

In Ceylon the extraction of graphite is carried out largely by the hand labour of the natives and only at the more important mines is the material raised by means of power-driven pulleys and the water withdrawn by means of steam pumps. The graphite is suitably screened before packing in barrels for transit.

In other countries, where the graphite is more impure, a more careful mechanical screening and a chemical purification are carried out, graphite containing as muchas 20 to 25 per cent. of gangue (ferric oxide, silica, ferric sulphide, clay, etc.) being thus utilisable. Winkler treated the material first with fused caustic soda and then with hydrochloric acid and water. Bessel mixed the graphite with petroleum (or resin oil, wax, etc.), and then with hot water (at 30° to 40°) and 1 per cent. of powdered calcium carbonate, mixed the mass and then added dilute hydrochloric acid; the bubbles of CO_2 carry the finer graphite particles to the surface, so that these can be separated; by this means an enrichment of 60 to 90 per cent. is attained. Langbein (1898 and 1900) treats the graphite with concentrated sulphuric acid, which heats it and also attacks the clay, forming aluminium sulphate capable of utilisation; it is then treated in an autoclave with concentrated caustic soda solution, which dissolves the silicates as sodium silicate, this also being utilisable. If resistant silicates (mica, etc.) are present, ammonium fluoride is added to the sulphuric acid used, the hydrofluoric acid liberated attacking the silicates with liberation of gaseous silicon tetrafluoride, which yields ammonium fluoride again if passed into ammonia; the ammonium sulphate remaining in solution is also utilisable. Like Bessel, Putz (1901) treats the graphite with petroleum and water, and then places the mass in bags immersed in running water, which carries away the petroleum and water and leaves only the graphite in the bags; this is drained and pressed hydraulically.[1]

LUBRICATING GRAPHITE in a very fine state of subdivision was prepared by Brody in 1865 by treating powdered graphite with about 7 per cent. of potassium chlorate and 200 per cent. of concentrated sulphuric acid in iron vessels, the mass being well stirred and heated in a water-bath until evolution of chlorine ceases. The cooled mass is poured into a

[1] Graphite rich in sulphur and oxide of iron (at a high temperature the latter attacks the graphitic carbon) has sometimes to be purified. For this purpose Ed. Donath (1916) heats the graphite in covered crucibles with rather more than the necessary amount of zinc dust ($R_mS_n + Zn_4 = R_m + Zn_4S_n$; $Fe_2O_3 + 3Zn = Fe_2 + 3ZnO$) and heats this mass with concentrated hydrochloric acid, hydrogen sulphide being thus liberated; subsequent washing with water removes the iron, while the zinc is evaporated earlier during the heating. In certain difficult cases sulphur and iron may be eliminated by making the graphite into a paste with concentrated caustic soda solution and treating in the hot with permanganate until a persistent violet coloration is obtained; after treatment with hydrochloric acid and then with water the purified graphite remains (graphite containing 3 per cent. of sulphur and 5 per cent. of oxide of iron shows after the above treatment 0·34 per cent. S and 0·55 per cent. Fe_2O_3).

large amount of water and thus thoroughly washed, being afterwards dried and heated; the graphite swells and is converted into a very fine powder which at the end is levigated with water. If the crude graphite contains much silica, sodium fluoride is added with the chlorate. In the Luzi process the graphite is moistened with concentrated nitric acid and heated in iron retorts, most of the nitric acid being thus recovered and the pure swollen graphite separated from the gangue; the mass is washed and levigated and then compressed.

Artificial graphite is to-day prepared in large quantity, more especially for the manufacture of electrodes employed in electrochemical industries, which have to be very resistant to the most energetic chemical agents. The process which is most used is that of Acheson (U.S. Pat. 568,523), who obtained the graphite as a secondary product in the preparation of silicon carbide (*carborundum*), using as carbon petroleum coke mixed with pitch and silica or iron oxide. The latter substances act at a temperature above the evaporating point of their carbides as catalysers, and transform large quantities of carbon into graphite. When the graphite is to be used for pigments or for crucibles, anthracite is used as the source of carbon. The International Acheson Graphite Company work with power from the Niagara Falls in furnaces formed by channels of refractory material 9 metres long, lined internally with carborundum. The charge consists of 3 to 3½ tons of carbon, and an alternating current of 1500 amps. at 210 volts is passed through from the ends; in the course of a few hours the current is raised to 3600 amps. and the temperature of graphite formation is then reached and is maintained for twenty-four hours. As the temperature gradually rises the conductivity increases and the current passing rises to 9000 amps. whilst the voltage descends to 80, so that about 1000 h.p. is used.

Acheson (1908–1909) discovered that graphite may be subdivided to an extraordinary degree by the process of deflocculation, which consists in suspending finely powdered pure graphite in water containing tannin and a trace of ammonia or, better, in mixing this aqueous emulsion with oil in the hot; after a short time the graphite passes completely into the oil in the deflocculated state, forming a true colloidal solution of graphite in oil, this being sold as *oildag* and serving as an excellent lubricant.

The particles of deflocculated graphite were studied under the ultramicroscope by Freundlich (1916) and found to have diameters varying from 2 to 6 μ (micron) to 500 $\mu\mu$ (submicron).

STATISTICS AND PRICES. Commercially a natural graphite is regarded as good if it contains 90 to 96 per cent. C, medium with 70 to 80 per cent., and inferior with 40 to 50 per cent.[1]

Ordinary graphite either powdered or in cakes costs about £6 per ton, whereas that from Ceylon which, owing to its fibrous structure, is especially suited for making crucibles and

---

[1] The carbon content is usually determined by fusing a mixture of 0·5 gram of the powdered graphite with 25 grams. of litharge in a porcelain crucible and, after cooling, weighing the lead separated (34·5 parts Pb correspond with 1 part C). A more exact method consists in combustion in the calorimetric bomb (*see later*, p. 461) in oxygen at 25 atmos.; as suggested by F. Mayer (1911), 0·6 gram of the graphite is mixed with 0·4 gram of pure benzoic acid to facilitate the complete combustion, the result being corrected for the heat due to the benzoic acid (6322 cals. per gram) and then calculated on the basis of 7900 cals. per gram of graphitic carbon. If the graphite contains sulphur, the bomb will contain sulphuric acid, which may be collected and titrated, 7·06 cals. being deducted from the result for each c.c. of decinormal alkali used in the titration.

The percentage compositions of some of the commoner graphites are as follows:

	Volatile products	Carbon	Ash
Cumberland, very good	1·10	91·55	7·35
,, ordinary	3·10	80·85	16·05
Passau	7·30	81·08	11·62
,,	4·20	73·65	22·15
Ceylon, crystallised	5·10	79·40	15·50
,, , common	5·20	68·30	26·50
Graphite from Creusot iron	—	90·80	9·20
,, ,, Givers iron	—	84·70	15·30
Madagascar	5·18	70·69	24·13
Brussin (Department of Rhone)	0·28	92	7·72
Urals	0·72	94·03	5·25

for use in the steel and bronze industries is sold at £20 per ton. In the United States an inferior quality is used for the adulteration of superphosphates, etc.

The price of graphite, especially of Ceylonese, is rapidly increasing, as the deposits being worked are gradually becoming exhausted; thus the price per ton was £18 prior to 1910, £38 in 1913, and £50 in 1914. Production, etc., is shown in footnote.[1]

FUELS

Carbon in its commonest form, *i. e.*, as coal, is of immense importance in the whole social and industrial economy as a fuel, that is, as a valuable and economical source of heat. Of the different fuels: gaseous [illuminating gas, marsh gas (methane), hydrogen, carbonic oxide, poor gas, water gas, acetylene], liquids (petrol, alcohol, mineral oils, etc.) and solid

---

[1]

Country	Year	Production		Importation		Exportation	
		Tons	£	Tons	£	Tons	£
United States . .	1904	2,300	35,440	14,000 Ceylon			
	1906	2,700 crys.		25,000 ,,			
	1906	22,800 amorp.					
	1908	1100 crys.	26,560	11,400 ,,	152,000		
	1908	1,440 amorp.	15,000				
	1910	3,800		22,000 ,,	374,400		
	1911	2,200 cryst.	53,000	18,000 ,,	300,000		
	1911	1,100 amorp.	6,400				
Germany . .	1904	3,784	8,400	2,628			
	1905	4,921					
	1907	4,033					
	1909	6,774		29,191		2387	
	1910	7,415		30,733			
Madagascar . .	1912	2,732				2732	
	1913	6,314				6314	
Canada . . .	1907	525					
	1909	864	960				
Italy . . .	1903	7,920	6,000				
	1906	10,800		360		4900	
	1907	11,000	12,800	240			
	1908	12,900		383	7,665	7009	22,428
	1909	12,500	14,000	140	2,810	8125	27,626
	1910			229		7647	
	1911	12,621	15,360	247	4,930	7633	25,952
	1912	13,170	15,870	402	8,055	7784	
	1913	11,145	13,160	567	11,348	8329	28,319
	1914	8,567	10,395	162	2,264	7589	27,320
	1915	6,176		1,506	45,177	6508	26,032
	1916	8,182		1,071	32,142	5615	22,460
Norway . .	1906	2,110	1,180				
	1908	1,150	2,600				
Ceylon . . .	1904	29,000	422,000	. . . .	. . .	Whole output exported	
	1906	40,000	680,000				
	1907	33,000					
	1908	28,200					
	1909	28,000	520,000	. . . .	. . .	,,	
Austria-Hungary .	1905	37,000	54,800				
	1907	40,000					
	1908	48,000					
	1909	45,000	64,000				
India . . .	1907	2,470					
Mexico . . .	1907	3,200					
	1908	1,700	5,600				

The production of *artificial Acheson graphite* in the *United States* was as follows: 73 tons in 1897, 390 in 1900, 1500 (£44,000) in 1904, 2208 in 1906, 3350 in 1908, 6000 (£188,000) in 1910, 4500 (£140,000) in 1911, and about 6000 (6000 h.p. being used) in 1912.

In 1908 in *Italy* 1600 tons (£15,640) of artificial graphite were made in the form of electrodes and in 1913 a factory for making deflocculated lubricating graphite was erected at Novara by the Acheson Company.

Italy imported the following quantities of electrodes and prepared carbons:

	1910	1911	1912	1913		1914	1915	1916	
Tons .	454	544	866	1502	(£11,080)	1236	739	2060	(£329,520)

and carbons for arc lamps, batteries and dynamo brushes:

Tons .	930	988	1119	1001	(£24,033)	989	389	220	(£12,310)

England imported 16,645 tons of graphite crucibles in 1909, and 16,386 tons in 1910.

France imported 3796 tons of graphite and plumbago in 1913, 4626 in 1914, and 5053 in 1915; also 660 tons of prepared carbons for electric lamps in 1913, 301 in 1914, and 564 in 915, the exports being 5947 tons in 1913, 4392 in 1914, and 2316 in 1915.

(wood, coal, fats, etc.), coal is the most important, whether as a fossil product (ordinary coal, lignite, etc.) or as coke or residue from the distillation of different fuels. Wood and coal may be considered as true storehouses of solar energy. Coal especially is but a great accumulation of solar energy of a very far distant epoch, since there is no doubt that coal was formed by the slow decomposition of enormous quantities of plant residues buried under heavy layers of rock. The imprints which have been discovered in blocks of coal by means of suitable chemical treatment, aided by the microscope, have also shown that at that time certain regions were covered by dense forests of gigantic conifers. Through the enormous pressure, terrestrial heat, water vapour, and in all probability through the successive interventions of special micro-organisms,[1] these buried vegetables—composed mainly of cellulose,

---

[1] **Origin and Composition of Coal.** According to Petzholdt (1882), the transformation of wood into coal must have taken place under the action of the heat produced by the enormous pressure of the superposed geological strata, this producing a kind of distillation under great pressure with softening of the mass until the vegetable fibrous structure is lost; with subsequent hardening the coal assumes an amorphous aspect with a conchoidal fracture similar to that of many compact, amorphous substances which have undergone fusion. Both Petzholdt and also Violette and Potonié have shown that, when wood is heated in closed vessels under high pressures, it softens, loses its structure and yields a product similar to coal.

E. Bergius (1912) succeeded in preparing coal containing 83 to 84 per cent. of carbon in the laboratory by heating peat (with 80 per cent. of water) or wood under great pressure with eight times its weight of water in a bomb at 340° for eight hours; the same degree of carbonisation of wood was reached by heating only at 310° for sixty-four hours and, on the assumption that in nature the carbonisation of wood has taken place in presence of water at 10°, it is calculated that the conversion of wood into coal must have required about eight million years, which coincides fairly well with the results of geological investigations.

One of the intermediate or final phases of the decomposition of the cellulose of wood has undoubtedly been brought about by anaerobic bacteria, viz., *Micrococcus carbo, Bacillus carbo, Micrococcus petrolei*, etc. (Renault). According to Omelianski (1906), the principal participants in the fermentation and decomposition of cellulose are two sporogenous anaerobic bacilli resistant to 90°, the more active of these producing methane and carbon dioxide and the other hydrogen and carbon dioxide.

F. Fischer (1899) states that coal decolorises bromine water, so that it contains unsaturated organic compounds which fix the bromine and partially liberate HBr; coal also absorbs oxygen, evolving CO_2 and H_2O, and this is sometimes the cause of the spontaneous ignition of coal in mines. Such ignition has been often attributed to the action of bacteria or to the presence of oxidisable ferric sulphide (pyrites), but the ease with which coal gives very fine dust and the readiness with which this oxidises and becomes heated to ignition cannot be denied.

With ozone coal appears to give marked quantities of products soluble in water (?). As a solvent for organic compounds already formed in coal Guignet (1879) and Frazer and Hoffmann (1912) used phenol and obtained complex hydrocarbons; if phenol is used at 100° (Poar and Hadley, 1915), the residual coal no longer gives coke. Various other neutral, acid, and alkaline solvents have been tried without it being possible to identify the products extracted, although from that obtained by Donath and Manouscheck (1908) by means of carbon disulphide, anthraquinone of a yellow colour (soluble in conc. $NaOH$) was formed by simple oxidation with chromic anhydride, the presence of anthracene in the coal being indicated. In 1894 Bedson used aniline as solvent and in 1899 and 1908 he showed that the best solvent is pyridine (it extracts up to 30 per cent., *i. e.*, almost the whole of the volatile products, the residue always being devoid of the power to form coke). The pyridine combines, however, with part of the compounds extracted and during the extraction in the hot the powdered coal swells markedly; this may be avoided (according to A. Wahl, 1912) by mixing it with anhydrous $NaCl$ or Na_2SO_4. Quinoline sometimes extracts four times as much as pyridine at the same temperature. Micrographic examination (*see*Iron), applied by Wahl and Bagard (1913), gives no information as to the components of coal. The hydrocarbons (benzine, benzene, toluene, etc.) are not good solvents, although Pictet and Lamseyer (1911) extracted with benzene a well-defined substance, viz., hexahydrofluorene; pyridine extracts substances which have the same composition as coal (but distil completely) and form two groups: humous substances with less than 5 per cent. H and resinous substances with more than 5 per cent. H. Hexahydrofluorene they obtained also from the tar (4 per cent.) resulting from the distillation of coal in a vacuum at 450°. In Germany, during the European War, mineral oils were extracted from coal by treatment with liquid SO_2. Burgess and Wheeler (1911) and Vignon (1913) studied the products of the direct distillation of coal at various temperatures and found that below 600° the unsaturated hydrocarbons distil over almost completely, at 600° to 800° the bulk of the saturated hydrocarbons (methane, ethane, etc.), and at 800° to 1000° almost all the hydrogen, a little saturated hydrocarbon, and a little CO, while above 1000° the gases contain much CO.

Pictet and Bouvier (1912–1914) and Burgess and Wheeler (1914–1915) studied systematically the *vacuum tar* obtained by rapid distillation of coal below 450° under reduced pressure (15 mm. of mercury). When freshly distilled, this tar forms a mobile, translucent, brownish liquid with a slight greenish fluorescence and an odour of petroleum; it is lighter than water, but after a few days becomes heavier than water (even if kept in a vacuum). When fresh it gives up nothing to caustic soda and hence contains no phenols (*see* Vol. II., "Organic Chemistry": Distillation of that is, of hydrogen, oxygen, and carbon—gradually lost hydrogen and oxygen during a period of several hundred thousand years, thus becoming enriched in carbon: peat and lignite, which were formed after the cretaceous epoch, contain 60 to 70 per cent. of carbon. In the older strata, before the cretaceous epoch, we find enormous deposits of common coal containing 90 per cent. of carbon, and, the most ancient of all, deposits of anthracite containing 96 to 98 per cent. of carbon. Thus we are to-day consuming solar energy which was stored thousands of centuries ago, because a great portion of this was utilised in the growth of vegetable organisms. It has been calculated that every hectare (2·47 acres) of pine and fir woods grows 3½ tons of fresh wood each year, and we know that there are 4,500,000 hectares of forest land in Italy, 20,000,000 hectares in Sweden, 200,000,000 in the United States of America, and 323,000,000 in Canada. We may thus form a vague idea of the enormous annual accumulation of solar energy stored up by plants. We may also estimate this directly in calories by remembering that 1 kilo of wood furnishes, on burning, about 2800 cals. We may also note that only about 5 per cent. of the total solar heat is utilised by plants, whilst all the rest is utilised in heating the atmosphere, the soil, water, and all the various terrestrial bodies.

The treasure in the form of fuel which was produced in the bowels of the earth, and by which we profit daily, is truly enormous, and during the nineteenth century, through the marvellous development of industry, the consumption gradually increased to surprising proportions, this increase accompanying the progress of the enormous and various works for which it is a vital necessity.

PEAT

In the natural formation of coals, peat may be regarded as the most recent decomposition product of immense layers of herbaceous plants, algæ, and rushes which still show clearly their structure and external habit (*Phalaris arundinacea, Aira cespittosa, Scripus, Carex, Cyperus florescens*, etc.). That formed in deep deposits has lost all structure and has an almost shining appearance, so that it is sometimes confused with brown or earthy lignites.

It occurs in large deposits in marshy districts in various countries (*see later:* Statistics), is very wet (60 to 95 per cent. of water), and after being dried in the air still contains 25 to 40

Tar), but these are gradually formed, spontaneously and in abundance, in the mass. Dilute hydrochloric acid extracts only 0·5 per cent. of pyridine and quinoline bases (dehydromethyl- and dehydrotrimethyl-quinoline, $C_{19}H_{11}N$ and $C_{12}H_{15}N$). It contains further unsaturated cyclic alcohols: paramethylcyclohexanol, $C_7H_{14}O$, besides $C_8H_{10}O$, $C_9H_{12}O$, $C_{10}H_{14}O$, and $C_{11}H_{16}O$; all these alcohols are insoluble in dilute caustic soda, but they become soluble after some days owing to their isomerisation and polymerisation to phenols. When vacuum tar is distilled over metallic sodium, the alcohols and phenols are fixed and only the hydrocarbons distil, the unsaturated ones being removed by dissolving them in liquid sulphur dioxide. The residual saturated hydrocarbons are divided into two parts according as they do or do not distil in steam, but with permanganate they all yield fatty acids of the paraffin series and not of the true benzene series, so that those hydrocarbons which have the general formula C_nH_{2n} (from C_9H_{18} to $C_{13}H_{26}$) belong to the hydrobenzene series (*e. g.*, hexahydromesitylene, $C_{10}H_{20}$). At a high temperature these cyclohexanes or hydrobenzenes lose hydrogen and methane (which occur in illuminating gas) and form stable benzene compounds (benzene, toluene, naphthalene, etc.) which are found in ordinary coal-tar. Vacuum tar does not contain naphthalene (so abundant in ordinary tar), but if the cyclohexanes are passed over heated coke, much naphthalene, benzene, and diphenyl are obtained. These cyclic hydrocarbons of vacuum tar were separated by Pictet, Ramseyer, and Kaiser (1916) directly from coal by extraction with boiling benzene and were found to be optically active (feebly lævorotatory, like petroleum). Vacuum tar hence contains unaltered the compounds found in coal (excepting the optically active ones, which are racemised: *see* Vol. II., "Organic Chemistry"); Berthelot's old hypothesis—according to which coal at high temperatures forms acetylene and this in contact with the hot walls of the retort polymerises forming the various aromatic hydrocarbons of ordinary tar—is thus refuted. The predominance of cyclic compounds in coal (even the coke remaining after distillation in a vacuum yields, on energetic oxidation, cyclic acids, *e. g.*, mellitic) leads to the supposition that the cellulose of wood, which is the prime material from which coal is derived, has a cyclic structure.

J. Harper (1914) considers that the nitrogen evolved as ammonia during the distillation of coal is derived from the nitrogenous side chains of the coal molecule, whereas the nitrogen remaining in the coke forms part of the cyclic structure.

Donath (1911) shows that, when coal is distilled in presence of nitric acid, the distillate contains no trace of hydrocyanic acid, which is, however, obtained from lignite under the same conditions.

per cent. of water,[1] 3 to 15 per cent. of ash, and 5 to 40 per cent. of humic acid. When it contains more than 25 per cent. of ash (sand, earth, etc.), it is not convenient to utilise it as fuel.

One cu. metre of moist brown peat, just extracted, weighs 900 to 1000 kilos, whilst with spongy peat or that dried in the air the weight is 200 to 300 kilos, and with highly compressed peat 600 to 800 kilos. A good air-dried peat has a calorific value of 3000 to 3500 cals., or, when pressed and dried at 100°, 4500 to 5000 cals.[2]

When distilled from retorts, air-dried peat leaves a residue of 40 per cent. of *peat coke* and 60 per cent. of volatile products (including water) which largely condense, giving a dense tar often rich in paraffin wax (about 4 per cent. of tar, 0·45 per cent. of acetic acid, 0·15 per cent. of ammonia, 0·3 per cent. of methyl alcohol, 0·3 per cent. of paraffin wax, 1 per cent. of phenols, etc.).[3]

The improvement of peaty lands has assumed great importance in some countries, notably Germany and Holland, where the surface peat has been removed and utilised in various ways (*see later*) and the residual earth drained and rendered highly fertile with manures from town refuse as well as chemical manures.

Spontaneous drying of the fresh wet peat is very slow, and various methods and plant have been devised to dry and compress the peat into bricks, so as to render it more compact and more economically transportable.

Some years ago attempts were made to prepare compact bricks directly by compressing the peat with powerful hydraulic presses (2000 atmos. or more), but under high pressures the peat largely escapes as a gelatinous paste through the coverings of the bricks, and little water is removable in this way. Since Eckenberg's investigations (Ger. Pat. 169,117) compact briquettes of high calorific power have been obtainable: the mass is subjected to gradual heating to 200° in suitable apparatus or drums with recovery of the heat, the mass thus obtained being heated in presence of steam and thus converted almost into a dense paste, which is cooled and hydraulically compressed to blocks of density 1·29 to 1·35. These have a shining, black appearance, since during the heating there is formed an agglomerating paraffin wax-like substance, which renders the blocks impermeable to water, although about one-half of the original moisture is still present; the calorific power rises to 4000 cals. and may exceed 4500 if the bricks are exposed to the air for a few days so as to reduce the moisture content to 25 per cent.

Elimination of the water may be facilitated also by addition of magnesium chloride, but it is best to heat the peat a little to 160° and then to compress it.

From 30 to 35 per cent. of the water has been removed from peat by the electro-osmotic process of Schwerin and Meister Lucius and Brüning (Ger. Pats. 124,529 of 1900; 124,510, 128,085, 131,932, 150,069, 163,549, 166,742, 179,086 and 179,985 of 1902, and 185,189 of 1903), based on an old observation of Quincke, according to which the solid particles of an aqueous suspension are displaced in one sense, whereas the water goes from the positive to the negative pole. A pasty mass of the comminuted peat is placed in layers 40 mm. thick between the electrodes and subjected to the action of a continuous current of 1000 amps. per sq. metre of electrode surface; the water separates at the lower negative pole, whereas the block of

---

[1] In 1909 Eckenberg showed that, under the microscope, the detritus of peat is seen to be coated with a transparent colloidal layer of hydrocellulose. It is this layer which renders difficult and very slow the drying of peat in the air; the gelatinous coating is eliminated in time especially in seasons of alternating frost and warmth, or more rapidly by heating the moist peat to 170° to 200°. Peat which has been frozen is depreciated, as it breaks too easily. Drying in the air occupies several months, is incomplete in rainy places and requires much space and labour to spread the clods out in a single layer.

[2] If the peat is on the surface, drainage channels for the water may first be dug, so that the peat partly dries and becomes more compact, and may be removed with special ploughs and with spades and drags; the blocks are then arranged chessboard fashion to facilitate air-drying. When the layers are variable in thickness and the blocks cannot be dried on the spot, a homogeneous mass is obtained by spreading the peat on a hard pavement covered lightly with straw, treading and beating it for some time so that some of the water is eliminated, and dividing the homogeneous layer 20 to 30 cm. deep into blocks, and drying these as above; this product, however, tends to become powdery.

[3] The distillation products of the peat of Eastern Frisia (Germany) are, on the average, as follows: 35·12 % of coke, 2·79 % of tar, 29·66 % of tar water, and 31·12 % of gas; the coke contains 88 % C, 5 % H, 1% N, 1·02 % S, and 3·57 % ash. On distillation, the tar yields: 35·09 % tar oil, 55·12 % paraffin oil, 4 % coke, and 4·03 % gas. The tar waters contain 0·74 % of methyl alcohol, 0·0015 % of formic acid, 0·95 % of acetic acid, 0·001 % of propane, 0·0024 % of butyric acid, and 0·35 % of ammonia. The gas from the first distillation of the peat is composed of 27·43% CO_2, 2·23 O, 2·25 N, 8·60 CO, 14·3 CH_4, 1 S and 23·6 H, and has the calorific power 2700 cals.

peat with only 60 per cent. of water (in place of the original 90 per cent.) remains adherent to the upper positive pole. A plant of this type has been erected at Schwenzelmoor in East Prussia.

The block is still plastic, but is stiff and dries well in the air or by means of waste heat until it has only 15 to 20 per cent. of moisture; it is then sold in sheets or lumps under the name of *osmon* and burns well, with very little smoke, no slag, and little ash.

An analogous process is that of Morsey-Pickard and Verschner (Ger. Pat. 200,565, 1906). The peat is disintegrated to render it homogeneous and then sieved and dried in an oven with flat, horizontal plates (sometimes like the Herreshoff pyrites burners, *see* p. 295) and passed to the trucks which feed the press, similar to that shown for the preparation of coal briquettes.

M. Ziegler (Ger. Pats. 101,482 of 1897; 103,507, 144,149, and 175,786 of 1905) prepares a kind of *peat coke* by utilising the distillation products, and this has rendered the process remunerative in Germany and Russia; the furnaces are formed of two tall flat retorts, above of cast-iron lined with refractory material and below of fire-bricks. The charge consists of 20 tons of peat with 25 per cent. of moisture and the distillation is complete in eighteen hours. Besides the liquid products (tar, etc., *see above*), a quantity of superfluous gas is obtained for heating the furnaces, and the burnt gases from the furnace issue at 300° and serve for the preliminary drying of the peat after their temperature has been lowered (by mixing with cold air) to 80°, since fairly dry peat ignites at 140°; a fan which drives 800 to 1000 cu. metres of air at 80° into the drying chamber per hour removes as vapour 45,000 kilos of water per twenty-four hours, so that 150,000 kilos of peat in blocks with 50 per cent. of water can be dried to 20 per cent. The air issues from the drying chamber at 50° saturated with moisture. The coke from the retorts is in somewhat hard lumps containing little sulphur, and may be used for metallurgical purposes or for domestic heating (in small pieces); if the distillation is shortened, a kind of coke burning with a long flame is obtained. The coke from good peat has a calorific value of more than 7000 cals.[1]

USES OF PEAT. Besides as a poor fuel to be used on the spot or for glass or porcelain furnaces (as it gives a moderately pure flame), peat may be used as stable litter, as it readily absorbs and retains liquids and ammonia; it is employed also as a heat insulator. When washed repeatedly with dilute sodium carbonate solution and dried, it forms a soft fibrous mass which serves for making mattresses, cushions, wadding, etc. Successful attempts have been made to obtain from it alcohol and cellulose for paper-making.

Moist peat cannot well be used directly as a fuel owing to its low calorific value and to the fact that it damages the boiler-plates.

It is now demonstrated that the most rational and economical method of utilising peat consists in gasifying it on the spot in gas producers and using the gas for the production of electrical and mechanical energy, the ammonia formed being made use of separately (*see* pp. 361, 363). In the peat districts of Germany there are several of these electric stations using peat. A 10,000-h.p. station consumes annually the peat from 50 hectares (123 acres) 3 metres thick. The development of 1 h.p.-hour, by means of air-dried peat utilised in gas producers, requires the consumption of 0·9 to 1·35 kilos of peat, the gas obtained having a calorific value of more than 1000 cals. per cu. metre.

In Germany these stations have not always given satisfactory results, owing to the large proportion of moisture (up to 92 per cent.) in the peat and to the cost of transporting a material so poor and bulky. It may be treated in gas producers if the peat contains more than 1·5 per cent. N and the ammonia is utilised.

In some countries *peat charcoal* (a kind of coke; 100 tons of peat with 20 per cent. of moisture, yield 30 to 35 tons, worth 24*s*. to 32*s*. per ton) is prepared, together with: 1·5 tons of ammonium sulphate, 200 to 250 kilos of calcium acetate, 230 to 320 litres of methyl alcohol, 2 tons of tar oil, and 1·5 tons of cresylic acid.

STATISTICS AND PRICES. In *Italy* peat deposits occupy about 3000 hectares, and the annual output varies somewhat, according to the price of coal; 20,922 tons were produced in 1903, 59,440 in 1907, 33,325 (£13,430) in 1908, 88,000 in 1909, 39,700 in 1910,

---

[1] 100 kilos of peat with 35·3 per cent. C, 3·4 H, 0·7 N, 28·4 O, 31 H_2O, 0·1 S, and 0·9 of ash (calorific value 3792 cals.) gave: 273 kilos of coke, 4·5 of tar, 31·2 of tar liquor, and 37 of gas. When distilled, the tar gave 2 kilos of light oils, 0·7 of heavy oils, 0·3 of paraffin wax, 1·3 of phenates, and 0·29 of asphalte; the tar liquor yielded 0·34 kilo of methyl alcohol, 0·16 of ammonia, and 0·44 of acetic acid.

24,552 in 1911, 28,400 in 1912, 23,000 in 1913, and 33,305 (£12,900) in 1914. During the European War the scarcity of coal increased the output of peat, which reached 50,200 tons in 1915 and 67,550 in 1916.

In normal times the price of air-dried peat-blocks containing about 25 per cent. of moisture is 8*s.* to 9*s.* 6*d.* per ton at the works (5*s.* to 6*s.* 6*d.* in Germany and Sweden) and that of compressed blocks 11*s.* to 14*s.*

The surface occupied by peat in *Russia* is valued at 7 per cent. of the whole area, in *Finland* at 20 per cent., in *Sweden* at 12·5 per cent., in *Germany* at 4·24 per cent., and in *France* at 50,000 hectares (especially in the Somme, Oise, and Pas-de-Calais).

The output of peat in *France* was 80,000 tons in 1908, 78,600 in 1909, and 58,521 (£29,427, *i. e.*, 10*s.* per ton in 1913). In *Russia*, 944,640 tons were extracted in 1908 by 17,000 workpeople; in some years much more than this is obtained. The world's production is valued at about 10,000,000 tons per annum.

In *Germany* peat occurs abundantly on the coasts of the Baltic and North Seas, and also in Hanover and Bavaria, the total area being 2,850,000 hectares and the mean thickness 3 metres, corresponding with about 9000 million tons of peat. In some localities layers 100 metres thick are found.

In the *United States* 47,380 tons of peat were extracted in 1912, mostly for the recovery of ammonia. The Alaskan deposits still contain 11,200 square miles, or 12,900 million tons of peat.

LIGNITE OR BROWN COAL

This product also is formed by a process of moist putrefaction of wood which has been carried much further than in the case of peat. It is much more closely akin to ordinary coal, and although the xyloid lignites are distinguished from the latter by their woody fibrous structure and their brown colour, yet the German lignites and the Italian pitchy lignites often form compact, shiny black masses with no marked fibrous structure. It also contains less nitrogen, and when heated in a test-tube it evolves vapours of acid reaction (acetic acid), whilst coal gives vapours of alkaline reaction (ammonia or ammoniacal bases). Also when powdered lignite is heated with a solution of sodium hydroxide, the latter is coloured brown, whilst with ordinary coal it is not coloured (though certain Russian coals form exceptions). There are, however, some lignites which resemble ordinary coal in this particular.

Lignite and coal are distinguished more certainly by the Donath reaction: with dilute HNO_3 (1 : 10) in the hot lignite yields gas and colours the liquid red, whereas coal does not (lignin reaction).

Donath (1906) has advanced the hypothesis that lignite is produced from plants richer in lignin (*see* Vol. II., " Organic Chemistry ") than those which yield coal, and he does not, therefore, consider that lignite would in time be converted into coal.

A special quality of bituminous lignite, called *pyropissite*, which is found in certain deposits in Saxony and Thuringia, deserves mention. It is perhaps formed from oil-containing plants, and on distillation it yields very abundant oily products, especially paraffin wax. To-day, however, these deposits are almost exhausted, and it has been found that it is much more convenient to extract such lignites with a solvent, because larger quantities of paraffin wax of better quality are so obtained (*see* Vol. II., " Organic Chemistry "). The tar obtained by the distillation of bituminous lignites is distilled to produce paraffin wax. In Germany 600,000 tons of different lignites are distilled annually in 34 works (1907) using 1226 vertical retorts, more than 60,000 tons of tar or bitumen $[(a)_D = +10°]$ being produced.

Lignite is of widespread occurrence in various countries. It is very abundant in Germany (Saxony, Bavaria, Brunswick, the Rhine district, etc.) and in France (mouth of the Rhone). Important deposits of good quality are found in Bohemia, while Russia, England, and Denmark also contain considerable quantities of lignite.

In Italy, where there are but minimal quantities of other coals, lignite is comparatively abundant, and during the European War, when English coal was scarce and its price multiplied tenfold, all the lignite deposits were worked, including those not utilised in normal times owing to their inaccessibility. It is calculated that the Italian deposits still contain more than 100 million tons of lignite.

Different lignites have hardnesses varying from 1 to 3 on the Mohs' scale, and 1 cu. metre weighs from 800 to 1500 kilos. Dry lignite burns without swelling and with a bright, long, and only slightly smoky flame.

USES OF LIGNITE. The principal and almost exclusive use—direct or indirect—of lignite is as a fuel after it has been dried in the air—to reduce the moisture to 10·25 per cent., since when extracted it contains 30 to 50 per cent. of water, according to the quantity of ash (2 to 12 per cent.) and to the quality (xyloid, pitchy, bituminous); its calorific value varies between 3500 and 6000 calories. If it is to be used as a boiler fuel, its sulphur content must be determined, since this may be 4 to 6 per cent. or even 9 to 10 per cent., and may cause corrosion, although in good qualities it does not exceed 1 to 1·5 per cent. If ash and moisture are neglected, lignites contain 55 to 70 per cent. C, 5 to 6 per cent. H, and 20 to 30 per cent. O (25 to 40 per cent. of volatile products).

Much of the lignite, especially the brown German variety, is utilised rationally by compressing it in the hot (without tar or pitch, as the moisture is sufficient) to form briquettes (*see later*), which are suitable for domestic use, and have a calorific value of 4500 to 5500 cals. It is often distilled to obtain lignite coal or coke (also used to make briquettes or for metallurgical purposes) and lignite tar, which, when again distilled, yields paraffin wax, solar oil, etc. (*see* Vol. II., "Organic Chemistry": chapter on Paraffin Wax).

STATISTICS AND PRICES. In ordinary times in Italy the brown lignite of S. Giovanni Val d'Arno, dried in large lumps, is sold in trucks at the works at 8*s.* to 10*s.* per ton, and the pitchy lignite of Libolla at 13*s.* 6*d.* to 15*s.* per ton. In 1917, during the European War, pitchy lignite cost £6 and even £8 per ton, and in small lots as much as £12. The output is shown in the table below.[1]

COAL

This fuel is the ordinary coal used as a source of heat in both large and small industries, especially for steam boilers. It is found in various countries, but scarcely any occurs in Italy.

It is distinguished chemically from peat and lignite, since it does not give Donath's reaction and evolves alkaline vapours when heated in a tube.

Its specific gravity is 1·25–1·50 and 1 cu. metre weighs about 700–900 kilos or up to 1200 kilos, according as the lumps are of medium or large size.

Its elementary percentage composition lies between the limits: 80–95 C, 2·5–6·5 H, 0·3–1·5 S, 2·5–5 O, and 1–2 N. It is erroneous to think that the principal component of coal is free carbon. Coal is rather to be considered as a whole of varied and complex

---

[1] PRODUCTION OF LIGNITE IN MILLIONS OF TONS

	1898	1900	1903	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916
Germany (*a*)	31·6	40·5	45·8	52·5	56·2	62·3	66·5	68·4	69·1	73·5	82·3	87·5	84		
Austria (*b*)	21	21·5	22·1	22·7	24·2	26·3	26·7	26	25·1	25·6	26·5				
Hungary .	4·5	5·1	5·3	6·1	6·4	6·5									
Spain (*c*) .					0·189		0·233	0·265	0·246	0·710				0·328	0·473
France . .	0·530	0·683	0·689	0·709	0·739	0·765	0·749		0·710		0·751	0·793			
Italy (*d*) .	0·341	0·481	0·342	0·408	0·467	0·447	0·477				0·600	0·700	0·780	0·939	1·268
Russia . .								0·116	0·117						
Greece . .								0·009	0·004						
Serbia . .					0·211										
Bulgaria .					0·133										
Roumania .				0·130											

(*a*) Germany produces also large quantities of lignite briquettes: 14·8 million tons in 1909 and 19 million tons in 1912; 8 million tons of lignite were imported in 1909 and 6·98 in 1913. The reserve of lignite equals 8 milliard tons. Berlin alone consumed 2,200,000 tons of lignite in 1912.

(*b*) Exported 7 million tons of lignite to Germany in 1913.

(*c*) In the first half of 1917 the output was 296,780 tons.

(*d*) In 1917 the production was about 1,500,000 tons, and could have been increased but for lack of transport wagons.

chemical compounds resulting from the decomposition of the wood of the plants from which it is derived (*see above*). When distilled in retorts it yields mainly liquid and solid products of the aromatic series, besides methane and hydrogen and the solid residue of coke. The sulphur of coal is in the form not only of mineral sulphide (pyrites), but also of organic compounds. The solubility of the organic components of coal in various solvents has already been dealt with (*see above*). The gases included in coal comprise methane, ethane, ethylene, butylene, CO, CO_2, etc. Under the microscope coal often reveals the structure of the original vegetable fibres.

At almost all coal pits the coal has to undergo considerable preparation for the market. It is first of all graded by means of oscillating sieves of different mesh; the fine rubbish (*see* p. 361) obtained by this treatment contains up to 50–60 per cent. of ash and is utilised in various ways after it has been treated to separate various impurities by a method making use of their different specific gravities (coal 1·15–1·60, pyrites 4·8–5·2, earthy and mineral detritus 2–2·7); special sieves or oscillating planes are used and washing resorted to, the ash being reduced to 10–15 per cent.

A coal of good quality, *e.g.*, of the Cardiff type, loaded on trucks at Genoa, should not contain more than 10 per cent. of small coal passing through a 20 mm. mesh.

In a large accumulation of coal the temperature may rise from the inside of the heap to the outside until the coal *ignites spontaneously*. To the causes of such ignition recorded on p. 442 may be added the richness in bituminous substances of certain coals which, by simple exposure to inclement weather, especially in hot places, may lose 3–5 per cent. of their calorific power, whereas with ordinary coal the annual loss is 0·3–1 per cent. To remedy or prevent such losses, particularly in very hot countries, coal is sometimes kept under water, this also removing danger of ignition.

The Mond and Caro method of utilising coal for obtaining ammonia and gas for driving motors has been dealt with in detail on pp. 361 *et seq.*

The following more important qualities of coal are distinguished for industrial purposes:[1]

(1) *Fat coal*, which when powdered and heated in a crucible fuses together and forms a homogeneous mass of compact, fused coke. It is very rich in hydrogen and is easily lighted, giving a long flame. It is largely used for gas manufacture, as it yields 25–30 per cent. of gas.

(2) *Caking coal* is that which is more commonly used for boilers. When powdered and heated in a crucible, it gives a solid agglutinated mass which is, however, not fused, but forms a light and porous coke. Some of it gives little gas and some a good deal. It often contains a little iron pyrites and burns with a short flame.

(3) *Lean or dry coal* is the poorest quality. It contains much oxygen and little hydrogen. It costs less, is used for lime and brick kilns, etc., and burns with a fairly short flame.

The following table, showing the output and consumption of coal in different countries, gives an idea of the wonderful industrial development of the past twenty-five years:

---

[1] Grumer's classification is as follows:

(1) *Dry, long-flaming coal* has a plane or conchoidal fracture, is hard, contains 75–80 per cent. C, 5·5–4·5 per cent. H, and 19·5–15 per cent. O, and gives 50–60 per cent. of coke, which is pulverulent or almost so. (2) *Fat, long-flamed, or gas coal* has a lamellar fracture, contains 80–85 per cent. C, 5·8–5 per cent. H, and 14·2–10 per cent. H, and yields 60–68 per cent. of fused, spongy coke. (3) *Fat or forge coal* has a shiny, lamellar structure, is less hard than (2), contains 84–89 per cent. C, 5–5·5 per cent. H, and 11–5·5 per cent. O, gives 68–74 per cent. of fused and not very porous coke, and burns with a short, slightly smoky flame. (4) *Fat, coking coal* burns with a short, non-smoky flame, has a lamellar structure, contains 88–91 per cent. C, 5·5–4·5 per cent. H, and 6·5–5·5 per cent. O, gives 74–82 per cent. of slightly porous, compact fused coke, and has a high calorific value (more than 9000 cals.). (5) *Anthracite or lean, short-flaming coal*, does not catch fire easily, burns with a non-smoky flame, contains 90–93 per cent. C, 4·5–5 per cent. H, and 5·5–3 per cent. O, gives 82–90 per cent. of pulverulent or slightly fused coke, and has a high calorific power (above 9000 cals.). To the gas coals belong also cannel and boghead coals, which are only slightly lustrous, burn with a long, vivid flame, and are rich in hydrogen and poor in oxygen; they may be regarded as varieties of bituminous shales moderately rich in volatile substances, and are largely used to improve certain gas coals so as to obtain more luminous gas. They are obtained especially near Edinburgh and on distillation yield also paraffin wax and mineral lighting oil.

PRODUCTION AND CONSUMPTION OF COAL (IN MILLIONS OF TONS)

		1850	1880	1895	1900	1905	1908	1910	1911	1912	1913	1914	1915	1916	
Argentine	import.	—	—	—	—	—	—	2	—	—	—	—	—	—	
Australia	prod.	—	0·94 (1872)	4·36	6·49	7·62	10·6	11	—	—	—	—	—	—	
Austria-Hungary	prod.	1	6	10·8	13·4	13·7	13·9	14	14·9	15·6	16·3	15	—	—	Without lignite.
	import.	—	—	—	—	—	10	9·8	—	—	—	—	—	—	
Belgium	prod.	5·8	15·6 (1872)	20·45	23·48	21·77	23·6	24	22	—	—	—	—	—	In 1909 1·3 was imported to make coke, and 2·7 of briquettes were also made.
	import.	—	—	—	—	—	—	5·87	—	—	—	—	—	—	
	export.	—	—	—	—	—	—	5·08	—	—	—	—	—	—	
Canada	prod.	—	—	—	5 (1902)	9·5	10·9	11·4	—	—	—	—	—	—	
	consump.	—	—	—	—	13	—	—	—	—	—	—	—	—	
China	prod.	—	—	—	—	—	12	13	—	—	—	—	—	—	
France	prod.	4·4	19	27·6	32·7	35·2	37·6	37·5	38·6	40·4	40·1	—	—	—	In 1913 the imports were 3·7 from Germany, 11·3 from Great Britain, and 3·7 from Belgium.
	import.	—	—	—	—	—	—	—	—	—	18·7	15·4	19·1	—	
Germany	prod.	5	47	79·2	109·3	121·3	148·6	150	160·7	177·1	191·5	161·5	—	—	3·9 briquettes made in 1909, and 5 in 1911 and 1912 (1·5 exported). Import. 12·1 in 1909, 10·5 in 1913. Coal deposits 290 milliard tons to 2000 metres deep—75 certain, 153 probable, and 62 uncertain.
	export.	—	—	—	—	—	21·2	—	—	—	34·6	—	—	—	
	consump.	—	—	—	—	—	139	135	—	—	158	—	—	—	
Great Britain	prod.	65	149	192·7	228·8	239·9	265·7	264	271	260	287·4	265·6	—	—	
	consump.	—	—	—	165	169	—	185	—	—	—	—	—	—	
India (British)	prod.	—	—	—	5	9	—	13	—	—	—	—	—	—	
Italy	prod.	—	—	—	—	—	—	0·005	—	—	0·007	—	0·0093	0·0185	
	import.	—	1·74	4·30	4·95	6·5	8·4	9·3	9·6	10	10·8	9·8	8·4	8·1	
Japan		—	—	—	8	12	—	15·5	—	—	—	—	—	—	
Mexico	prod.	—	—	—	—	—	—	1	—	—	—	—	—	—	
Natal		—	—	—	—	1·5	1·7	2	—	—	—	—	—	—	
Norway and Sweden		—	—	—	—	0·30	0·31	0·303	—	—	—	—	—	—	
Portugal	prod.	—	—	—	—	—	—	—	—	—	0·008	0·045	0·060	0·084	
	import.	—	—	—	—	—	—	—	—	—	1·35	1·18	1·05	0·70	
Russia	prod.	—	3	9·1	16·1	18·7	24·5	23·1	26·6	—	—	—	—	—	The deposits in European Russia are estimated at 75 milliard tons, and those in Asiatic Russia at 175 milliards, besides 2·6 milliard tons of anthracite in the Donetz district.
	consump.	—	—	—	—	—	—	27	—	—	—	—	—	—	
Spain	prod.	—	—	—	—	3	3·9	4	—	—	—	—	4·136	4·847	In the first half of 1917, 2·322.
	import.	—	—	—	—	2	—	2	—	—	—	—	—	—	
Transvaal and Cape	prod.	—	—	—	2·5	2·7	3·0	4·0	—	—	—	—	—	—	
United States	prod.	8	66	175	244·6	386·3	380	415	493	512·9	—	—	—	—	Including 70 of anthracite in 1908, and 84 in 1912.
	import.	—	—	—	—	—	1·2	2	—	—	—	—	—	—	
	export.	—	—	—	—	—	12·7	14	—	—	—	—	—	—	
Total for whole world		90	302	511	—	990	1045	1140	—	1110	—	—	—	—	The total deposits are now estimated at about 8,400 milliard tons.

As regards the distribution of the coal used between different industries, in England about thirty years ago this was as follows:

For the production of iron and steel	30 per cent.
For heating and domestic use	17 „
For steam-engines	12 „
In ships	3 „
On the railways	2 „
In the mining industry	7 „
For gas manufacture	6 „
For the manufacture of glass and porcelain	4 „
In chemical works, breweries, distilleries, metallurgical works, excluding iron and steel, etc.	9 „
Export	10 „

These proportions are certainly changed nowadays.

The Coal Syndicate of Westphalia and the Rhine district distributed in 1910 nearly 66,000,000 tons of coal (including coke and briquettes) as follows: 42–45 per cent. for metallurgy, 13·22 for domestic purposes, 10·64 for railways and tramways, 7·18 for brick-works, 3·26 for making gas, 3·01 for chemical industries, 3·06 for textile industries, 1·07 for making beer and spirit, 1·46 for electrical industries, 1·04 for paper industry, 0·88 for the navy, 0·35 for the rubber and hide industries, 0·6 for sugar and glucose making, and 0·7 for the glass industry.

In Germany 427,000 workpeople were engaged in coal mines in 1905.[1]

RESERVE OF COAL. In view of the increasing consumption of coal throughout the world, which is not being arrested even by the large hydro-electric plants erected of late years (*see later:* Electro-chemistry), the question has often been asked if continuance of this pace would not rapidly and unconsciously exhaust the coal deposits, and hence ruin industry and lead to a terrible unknown future for the whole of humanity.

Technical experts and competent commissions have studied the problem, and from the calculations made in different countries it would appear that a prosperous future may confidently be expected, since in Belgium 23,000 million tons of coal still exist in the deposits, in England and Ireland at least 190,000 million, in Germany almost 300,000 million, in North America about 2,000,000 million, in France 19,000 million, in Austria 3000 million tons of coal and 12,000 millions of lignite to a depth of 1200 metres, and probably 25,000 millions of coal and 660,000 millions of lignite altogether, and in Russia 40,000 million tons. From these figures it can easily be seen how the first position as regards output of coal in Europe, up to the present held by Great Britain, will in the near future pass to Germany, while later Europe will become dependent on America, which has already begun to send coal to France and Russia.

ANTHRACITE. This may be regarded as a natural coke containing very little bituminous substances and very little hydrogen. It has neither a crystalline structure nor that of vegetable fibres, but is conchoid and irregular. It represents the oldest formation of coal, is fragile and blackish-grey-brown, and in the fire does not soften, but burns with a short flame and little luminosity. The composition of English anthracites is approximately: 1–2 per cent. ash, 1–3 per cent. volatile products, 0·6–1·2 per cent. S, 92–95 per cent. C; the calorific value is 7600–8200 cals.

When distilled it yields very little volatile products (gas) and much coke (82–90 per cent.), but this is not suitable for ordinary industrial uses (friable or powdery). To obtain complete combustion of anthracite requires a furnace with abundance of air and a strong draught.

---

[1] In 1900 the number of people employed throughout the world in mines (mostly coal mines) was 4,355,000; 875,000 in England, 500,000 in Germany, 445,000 in the United States, 320,000 in India, 310,000 in Ceylon, 293,000 in France, 240,000 in Russia, 219,000 in Austria-Hungary, 160,000 in Belgium, 119,000 in Japan, 60,000 in Italy (about one-half in the Sicilian sulphur works, many in the Sardinian mines, and part in the quarrying of marble at Carrara). Of 977,000 miners in England in 1907, more than 940,000 were employed at 3227 coal mines.

No consideration can be given here to the great progress made in the methods of extracting the coal or of constructing the galleries of the mines. Mention cannot be made of the advances made during the past century to render less irksome and safe from explosions the work of the miners.

As a less dangerous means of getting coal, the use of water pressure (up to 500 atmos.) has been suggested and in some cases applied, in place of explosives; further, special safety explosives are now made for use in mines (*see* Vol. II., " Organic Chemistry ").

Coal seams are found in different countries at various depths, ranging from 100 to 1300 metres below the surface. In Belgium the mines are usually 800–1000 metres deep and sometimes 1150 metres.

A large proportion of the anthracite obtained comes from *Great Britain* and still more from the *United States*, where the output in millions of tons was 66·8 in 1904, 71·4 in 1905, 65·5 in 1906, and 75 in 1908.

Spain produced 222,620 tons of anthracite in 1915, 268,087 (£320,000) in 1916, and 134,673 tons in the first half of 1917.

The price of anthracite is about 15 per cent. above that of ordinary coal, and before the war was 33*s.*–36*s.* per ton on truck at Genoa.

COKE is a hard, spongy form of amorphous coal and is a good conductor of heat and electricity; it is iron-grey and burns without smoke. It is used as fuel in small works and for domestic purposes, but is mostly employed in the metallurgical industries; part of it is converted in gas producers into water gas and suction gas (*see later*).

Formerly it was obtained almost exclusively as an abundant residue (prior to 1860 it often formed unutilisable refuse) from the distillation of coal in the manufacture of illuminating gas; the coke constitutes 60–70 per cent. of the coal used. This coke is, however, too spongy for metallurgical purposes—blast furnaces, etc.

The coke produced in gas-works cannot be used as metallurgical coke, as this must be free from volatile products and must consist as far as possible of pure carbon. It should be compact and hard, and therefore can be obtained only when the gases which are developed on heating (hydrocarbons) remain for a prolonged period in contact with the porous mass of coke which is formed. In this way the pores are partly filled by a graphitic mass. This is what occurs during the manufacture of metallurgical coke, but not during that of illuminating gas, so that the coke obtained during the latter process is not used metallurgically, in the same manner that the carbon obtained by the distillation of wood in retorts cannot be used instead of wood charcoal obtained in kilns for various metallurgical operations.

A good coal suitable for making metallurgical coke should contain 15–35 per cent. of volatile products and less than 8 per cent. of oxygen referred to the coal after the moisture and ash have been deducted. Since the oxygen in dry coal is transformed during distillation into water (of the ammoniacal liquor), CO_2 and CO, if a dry coal on distillation forms more than 8 per cent. of water it does not usually give a good coke. Coal exposed to the air for a few days, especially if fine, loses much of its property of yielding agglomerating coke, and the same happens if the coal has for any reason been heated to 200°. With some coals the quality of the coke formed is improved if the mass is compressed before introduction into the furnace chamber.

It would appear that in the preparation of metallurgical coke it would not be possible to recover volatile products of great value, as these would be consumed by the coke production itself. If one remembers, however, that of the products of distillation of coal those of greater value form only a small fraction of the whole mass, it appears possible to save the more valuable volatile products, whilst burning those of minor value for the production of coke. In order to obtain compact, hard coke without consumption of the more valuable volatile products, *coke-ovens* have been invented which are very narrow, very high, and very long, and are so constructed that the weight of the upper layers of coke, pressing on those below, hinders the swelling of the coal during heating, and a coke results which is less porous and more compact. From the vapours produced on distillation tar and ammonia are extracted, and the remaining gas is burnt in the regenerative furnaces, or, as is the case in many works, the benzene is first separated from these gases before burning them. This is done by cooling them strongly in order to condense the benzene, or by passing them through tar oils of high boiling-point, by which the benzene is dissolved (Franz Brunck's process). The benzene is then recovered from these solvents simply by distillation. By this process but little toluene is obtained, whilst more is formed by distilling gas tar. At one time only 5 per cent. of the benzene thus formed was condensed, but to-day, by means of this system of washing the vapours, the quantity of benzene has been trebled. Thus in Germany, where 15,000–20,000 tons of benzene were at first obtained, more than 90,000 tons were obtained even before the war. During the war the use of regenerative furnaces extended in all countries. In the chapter dealing with benzene and tar distillation (Vol. II., "Organic Chemistry"), more detailed descriptions are given of the processes of recovery of the by-products of the manufacture of coke and illuminating gas.

In Fig. 168 we give the general aspect of an old coke-oven which is charged from above and heated below by flues beneath the sole, in which the gases escaping from the distillation are burnt. Before being charged into the oven the coal is crushed, and then, after some days of heating, is discharged, as indicated in the figure, by means of a mechanical ram which enters at one door and forces the coke out at the other end, while still red hot; it is then quenched with water.[1] In Fig. 169 a battery of modern coke-ovens is shown in section, and in this we see that the charge is heated by means of a series of flues, *S*, S_1, in which the gas proceeding from the regenerator, *h*, is burnt. Above we see the tubes *i*, *k*, *l*, in which the gases and vapours obtained by the distillation of the coal are led away. As we see from the section, the chambers of these furnaces are 0·5–0·6 metre wide, 1·6–1·7 metres high, and 9–10 metres long. They take a charge of 5½–6 tons. In large works for the production of metallurgical coke, powdered coal is now used, together with small pieces. These are slightly moistened and are compressed into long and large blocks which have almost the dimensions of the furnace chamber. These blocks are carried, by means of a suitable car, up to the furnace, into which they are made to enter in such a way that the new block of coal which is forced into the furnace forces out the red-hot block of coke, which has just been finished, at the other end; if coal in lumps, and especially if rich in volatile products, were employed for making coke, a too spongy or friable product would be obtained. The heating of the coal for the production of coke lasts from 36 to 48 hours, and the yield of coke varies from 68 to 75 per cent., with simultaneous production of about 2 per cent. of tar and about 1 per cent. of ammonium sulphate. The most modern types of oven, which have lately become widely adopted for the recovery and utilisation of the vapours, gases, and tar, are the Semet-Solvay and Otto-Hoffmann ovens. In 1898 1800 Semet-

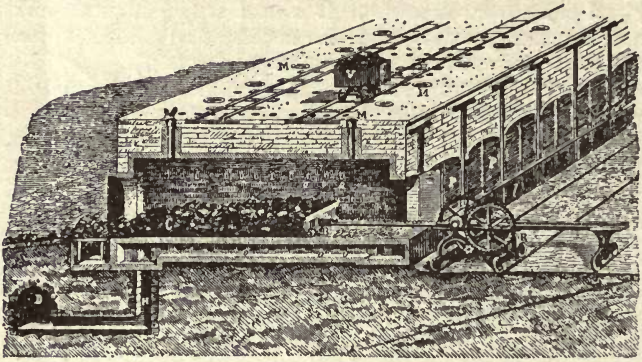


Fig. 168.

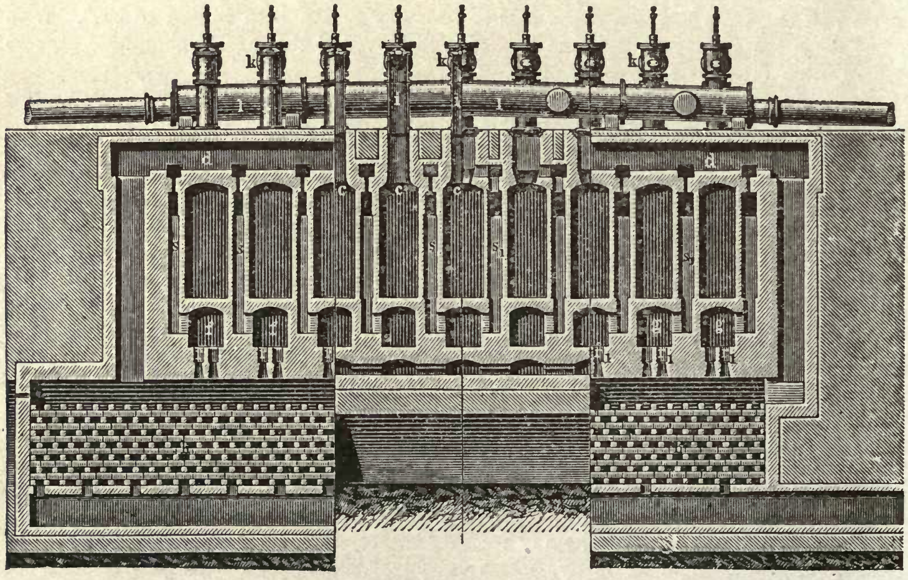


Fig. 169.

---

[1] It has recently been suggested that the coke be quenched in the retorts or chambers by means of steam, this leading to the production of water-gas, which has a certain value and utilises rationally the heat of the coke.

Solvay ovens were already at work in various countries, and there were also 5000 Otto-Hoffmann ovens at work in Europe, whilst in the United States alone 4000 Otto-Hoffmann ovens were constructed between 1902 and 1906. From 1906 to 1908, however, other ovens were more frequently constructed without regard to the recovery of the secondary products, as these could no longer be placed remuneratively on the market.

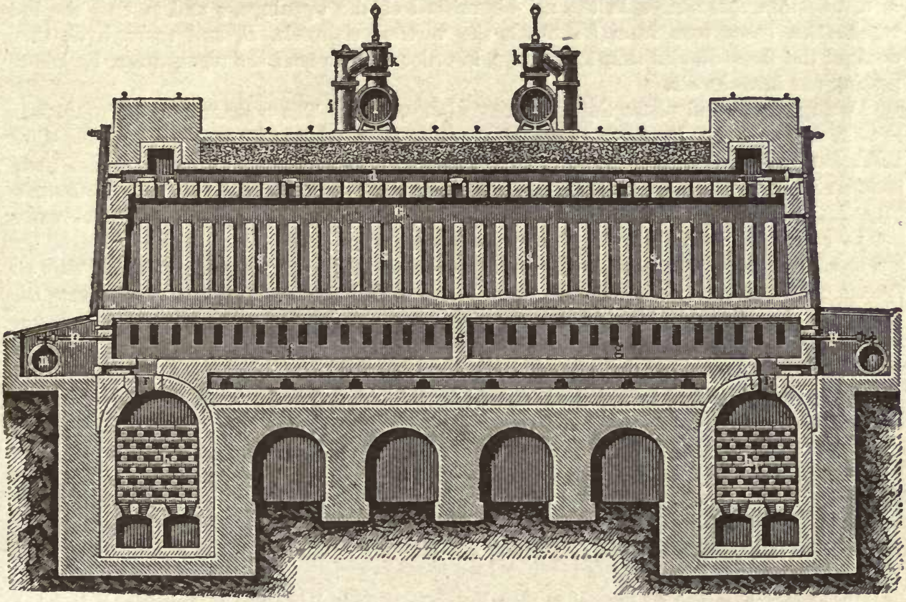


Fig. 170.

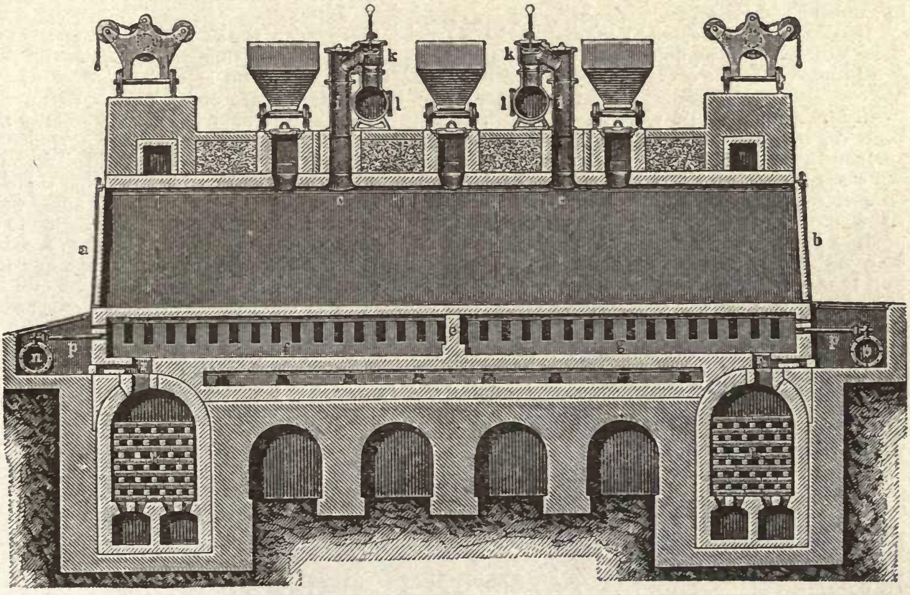


Fig. 171.

Figs. 170 and 171 give an idea of modern coke-ovens heated by means of Siemens' regenerating furnaces, *h* and h_1, of which we give a description in Part III in the chapter on Glass. *h* and h_1 are alternately used for heating the air which is required for the combustion of the purified gases proceeding at one period from *n* and at another from *o*. In the middle of the vaulted roof of each oven (Fig. 171) there are two large pipes, *c*, which carry away the gases, vapours, and tar formed on heating coal out of contact with air;

these are cooled in suitable condensers, such as are used in the manufacture of lighting gas. Each chamber is charged through three manholes above, the coal being carried on trucks. Between each oven and its neighbours there is a series of vertical flues, S and S_1, which lead upwards into a horizontal channel, G, and below into a channel divided into two halves, f and g. If during the first phase of the operations the air is heated in the generator, h, combustion commences in the neighbourhood of the openings, r and p, and the hot combustion gases pass from f through the vertical channels, S, and through G, then descend the flues S_1, and thus arrive in g, in order then to heat the regenerator, h_1, before passing out into the air.

During the second phase the gas current is reversed. The regenerator, h_1, now heats the air, and gas passes from g and through the flues S_1 and S into the regenerator, h. With this scheme of working there is no chance of any possible admixture of air and gas, as there is when these are able to pass through neighbouring regenerators, when they sometimes cause fusion of the material and explosions. Until now, preheating of the combustible gases has therefore not been applied. The regenerators are used only alternately for heating the air, of which a volume at least five times that of the combustible gases is required. This air arrives cold alternately through the tubes n and o, and is introduced alternately into the flues S or S_1. Since the air acquires a temperature of 1000° in the regenerators, it is not necessary to burn all the gas in order to work the ovens, and a part may be saved and used as a source of power. Air being completely excluded from the coke-ovens, the coke yields are 7 per cent. greater than those obtained in the old type of oven. In each chamber, charged with from 5·8 to 6 tons of coal, apart from gas used in heating, 100 cu. metres of gas of the following composition are now produced per day: Benzene, 0·6 per cent.; ethylene, 1·61 per cent.; H_2S, 0·42 per cent.; CO_2, 1·39 per cent.; CO, 6·41 per cent.; H, 52·69 per cent.; methane, 35·67 per cent.; water vapour, 1·21 per cent.; this gas may be used for lighting purposes or as power gas.[1] For the yields of tar, illuminating gas, coke, etc., obtained on distilling both coal and wood, *see* Vol. II., "Organic Chemistry."

---

[1] In France the first regenerative coke furnaces appeared in 1854 (Clovis Knab Patent), and in 1864 the first batteries of furnaces, improved by Carvès, who also erected the first plants in England and Spain.

In coke furnaces (heated by the distilled gases) without recovery of the heat (non-regenerative), the escaping hot gases, before passing to the flues, may be used for heating steam boilers, and it is calculated that for every kilo of coal distilled 0·85 kilo of steam can be obtained (from the hot combusted gases issuing from the furnace flues), so that distillation of 100 tons of coal per twenty-four hours would yield 85,000 kilos of steam in twenty-four hours, *i. e.*, 3540 kilos per hour, or, say, 482 h.p.

In furnaces where the heat is recovered (regenerative), 40 per cent. of the distilled gases can easily be saved, and, assuming that 1 ton of coal gives 280 cu. metres of gas (calorific value 3500–4000 cals. per cu. metre), this would amount to 11,200 cu. metres per twenty-four hours or 466·6 cu. metres per hour. Taking 800 litres of gas as the amount required by a gas engine to produce 1 h.p.-hour, the above quantity would generate 583 h.p., which is about 100 h.p. more than with a non-regenerative furnace. For a battery of thirty-six coke furnaces of the Carlo Still type, each of 7·5 tons capacity, one regenerator having a volume of about 127 cu. metres is required for each two chambers and 228 tons of firebrick (1 cu. metre weighs 1·8 tons) are required to fill one-half the volume, the other half constituting the interstices. With each furnace there correspond 3·5 cu. metres of regenerator.

The inversion of the current of hot gases and cold air in the two halves of the regenerator takes place every half-hour. The air from the hot regenerator may reach a temperature of 800°. To burn 1 cu. metre of coke-furnace gas requires about 5 cu. metres of air. In the Solvay furnaces, with channelled regenerators, the hot air reaches 600° and the combusted gases leave the regenerators at about 350°.

An installation of Otto-Hoffmann furnaces of ninety chambers, erected by the Hubertushütte Company (Germany), treats 320 tons of coal per twenty-four hours and gives an excess of 60,000–70,000 cu. metres of gas (calorific value, 3300 cals.), which is utilised in Martin (open-hearth) steel furnaces, and reduces the coal consumption in these from 318 kilos per ton of steel to less than one-half this amount. Each chamber of this installation holds 7·5 tons of coal, which is transformed into coke in thirty-six hours.

Before the European War coke-furnaces in which the by-products were recovered were general only in Germany, and it is this which allowed of the great development of the synthetic organic products industry (dyes, drugs, perfumes, etc.), and made it easy to procure the raw materials (benzene and toluene) required for the manufacture of shattering explosives, especially during the War. The proportion of such furnaces to the whole number in the United States was 5 per cent. in 1900, 16 per cent. later, and only 4 per cent. in 1909, it being found that no adequate and remunerative means existed of disposing of all the benzene produced; in England the proportion was 10 per cent. in 1900 and 28 per cent. in 1909, whereas in Germany it was 10 per cent. in 1900 and 82 per cent. in 1909.

Knab and Carvès were the first to construct, in 1856, a coke furnace for recovering the by-

The world's output of metallurgical and gas coke is shown below in millions of tons:[1]

Year	United States	Germany	England	Russia	Belgium	France	Austria	Spain	Italy	Canada	Whole World
1880	6·5	—	15	—	—	—	—	—	—	—	—
1900	18·63 + 0·6 (from gas)	—	—	2·24	2·44	2·29	1·23	—	—	—	—
1902	23·04	9·20	16	1·85	2·05	1·76	1·16	0·43	—	—	55
1904	21·47	12·3	19·61 + 11·8 (gas)	2·40	2·21	2·02	1·23	0·44	—	—	81
1906	35·02	20·27 + 3·5 (gas)	18·14 + 11·5 (gas)	2·26	2·41	2·28	1·68	0·44	0·030	0·70	85
1908	23·62 + 4 (gas)	21·18 + 4 (gas)	19·2	2·67	2·31	2·26	1·88	0·48	0·105	0·77	77
1909	35·6	21·4	19·6 + 13·1 (gas)	2·63	—	2·49	2·00	0·50	0·250	0·79	—
1910	37·81 + 4·5 (gas)	23·60 + 5 (gas)	19·7	2·75 + 0·8 (gas)	2·4 + 0·4 (gas)	2·69 + 3 (gas)	2 + 0·7 import. + 1·2 (gas)	0·60 + 0·5 import. + 0·5 (gas)	0·040 + 0·9 (gas)	0·81	90
1911	33	25·4	19·3	3·30	3·16	2·91	2·06	0·52	0·36	—	—
1912	40	29·1	—	—	—	—	—	—	—	—	—
1913	—	32	—	—	—	2·75 + 3·07 import.	—	—	0·500	—	—
1914	—	27·3	—	—	—	—	—	—	0·453	—	—
1915	—	—	—	—	—	—	—	—	0·449 + 0·823 import. + 0·816 gas)	—	—

products (tar, benzene, toluene, etc.) of the distillation of coal for manufacturing gas, the low calorific value of the latter—used to heat the furnaces—being counterbalanced by better utilisation of the heat, which had previously been partly lost by radiation and in the flue gases. Nowadays an excess of 40 per cent. of gas (*see above*) is obtainable. The gases are passed through channels to remove dust and tar, then through air or water coolers to recover the ammonia, and finally through heavy tar oils, which retain all or part of the benzene, toluene, xylene, etc. (*see* Vol. II., "Organic Chemistry"); the ammonia may also be fixed directly by means of sulphuric acid (*see* Vol. II.: Illuminating gas).

In the United States there were, in 1908, 101,218 coke furnaces and in 1909 103,982, the by-products (worth over £1,600,000) being recovered in 3989 of them.

In England there were 24,182 coke-furnaces in 1909 (22,983 in 1910), and in about 7000 the by-products were recovered. The numbers of the different systems were: With bee-hive ovens 17,393 (16,000 in 1910); Simon Carvès, 1143; Solvay, 842 (1055 in 1910); Coppée, 1959; Bauer, 52; Koppers, 408; Otto Hilgenstock, 948 (1025 in 1910); various others, 1437.

In Germany there were 18,883 coke furnaces with recovery in 1910, the 16,333 at work producing 822,617 tons of tar, 87,214 tons of benzene, and 313,195 tons of ammonium sulphate. In 1911 there were 19,903 coke ovens.

The Collin, Semet-Solvay, and Haldy types have horizontal heating channels, whereas the Coppée, Bauer, Otto-Hoffmann, Franc. Rexroth, etc., forms have vertical heating channels.

[1] Britain's exports were as follows (millions of tons):

To	1908		1909		1910		1911		1912	
	Coal	Coke	Coal	Coke	Coal	Coke	Coal	Coke	Coal	Coke
France . .	10·58	—	10·57	—	9·74	—	10·27	—	10·19	—
Germany .	9·80	0·053	9·82	0·068	9·15	—	8·97	—	8·39	—
Italy . .	8·88	0·062	9·23	0·069	8·92	0·054	9·22	—	9·18	—
Sweden .	4·44	0·148	4·03	0·170	4·05	0·162	3·83	—	4·12	—
Russia .	3·47	0·036	3·38	—	3·27	—	3·44	—	4·05	—
Denmark .	2·86	0·166	2·91	0·206	2·76	0·144	2·8	—	2·7	—
Spain . .	2·58	0·127	2·65	0·122	2·92	0·115	3·02	—	3·45	—
Egypt . .	2·54	—	2·65	—	2·60	—	3·10	—	3·44	—
Netherlands .	2·19	—	2·36	—	2·27	—	2·85	—	2·78	—
Norway .	1·97	0·124	1·93	0·125	2·01	0·140	1·97	—	2·20	—
Austria .	—	0·093	—	0·040	—	—	—	—	—	—
Greece .	—	—	—	—	—	—	0·68	—	0·61	—

In 1912 England exported 2,547,712 tons of anthracite, 46,539,983 tons of coal, 10,559,845 tons of gas coal, 1,026,021 tons of coke, and 1,565,432 tons of briquettes.

Italy consumed about 100,000 tons of metallurgical coke in 1903, 40,000 tons being furnished by the Savona works, and the rest imported from England, and, to a greater extent, from Germany. In 1913 the consumption in Italy was 870,000 tons, 370,000 tons being imported (one-half from Germany). The gas-works produced in 1908 nearly 709,000 tons of coke, which was used as an ordinary fuel. The output of coke (tons) in Italy was as follows:

	1910	1912	1913	1914	1915
Metallurgical coke	396,560	437,706	498,442	453,043	448,720
Gas coke	764,000	786,200	837,940	823,275	816,389

A good foundry coke usually has the following percentage composition: volatile products, 1; fixed carbon, 85·5; ash, 12; sulphur, 1·1, the water present being neglected. Complaint may be made if the coke contains more than 2·5 per cent. of volatile products, or less than 78·5 per cent. of fixed carbon, or more than 15 per cent. of ash or 1·3 per cent. of sulphur. It should be in large compact lumps without black edges and without slag; if the dust and small coke amount to more than 5 per cent., the seller should make an allowance on the price or weight, while if it is more than 25 per cent., the contract may be cancelled. The sulphur in coke may be reduced to 0·1 per cent. by heating the coke in presence of superheated steam and a little air.

In 1910 a Commission of the German Foundry Union fixed the following maximum

---

Germany's exports and imports of coal and coke (in tons) were as follows:

To or from	Year	Importation		Exportation	
		Coal	Coke	Coal	Coke
Belgium	1912	383,713	510,441	5,368,472	755,357
	1913	315,277	518,499	5,728,406	936,515
Denmark	1912	—	—	261,802	59,000
	1913	—	—	219,711	52,337
France	1912	—	22,414	3,057,502	2,275,000
	1913	8,064	8,943	3,242,175	2,354,918
Great Britain	1912	8,988,482	5,161	67,251	20,785
	1913	9,209,543	16,614	11,064	5,418
Italy	1912	—	—	724,482	167,513
	1913	—	—	892,463	183,456
Netherlands	1912	524,344	—	6,543,642	284,176
	1913	510,472	22,725	7,217,606	285,223
Norway	1912	—	—	56,659	47,350
	1913	—	—	19,170	44,492
Austria-Hungary	1912	474,860	29,143	11,015,315	965,800
	1913	492,610	24,153	12,152,500	1,051,670
Roumania	1913	—	—	131,002	19,347
European Russia	1912	—	—	1,510,501	421,935
	1913	—	—	2,103,210	546,191
Sweden	1912	—	—	95,688	204,978
	1913	—	—	177,656	208,107
Switzerland	1912	—	—	1,508,790	328,727
	1913	—	—	1,638,745	363,596
Spain	1912	—	—	160,027	37,010
	1913	—	—	279,015	37,276
Egypt	1912	—	—	83,127	—
	1913	—	—	90,003	—
Mexico	1912	—	—	—	51,248
Other countries	1912	4,057	1,722	338,585	322,872

The total amount exported in 1913 was 34 million tons of coal and 6·5 million tons of coke, while the imports were 10·5 million and 593,000 tons of coal and coke respectively. In 1908 Germany exported 3,577,496, and in 1909, 3,444,791 tons of coke.

The United States exported 879,000 tons of coke in 1910 and 914,000 tons (£640,000) in 1911. France imported 3,070,038 tons in 1913 (2,392,897 from Germany), 1,457,931 in 1914 (894,280 from Germany), and 224,936 in 1914 (from England and America).

In normal times the price of coke for blast-furnaces is 14*s.*–16*s.* per ton in Germany, England, and the United States, while that imported into Italy costs 22*s.*–28*s.* per ton.

An increase of 20 per cent. on the labour (wages) in Germany produces an increase of about 1*s.* 1*d.* on the cost price of coal.

limits for metallurgical coke: quality I, 5 per cent. water, 8 per cent. ash, 1 per cent. sulphur; quality II, 5 per cent. water, 9 per cent. ash, 1·25 per cent. sulphur.

WOOD CHARCOAL. This is produced by heating wood out of contact with the air in pieces and in logs in large heaps covered with earth. A few openings are left for the escape of the gases formed during the combustion. This is started by lighting the wood at the bottom; the process lasts several weeks, its completion being recognised by the colour of the smoke.

In this way all the volatile products, which are of great value, are lost, and to-day carbonisation is often conducted in suitable furnaces or retorts, which allow the volatile products, consisting of lighting gas, methyl alcohol, acetic acid, acetone, and tar, to be utilised. (*See* Vol. II., "Organic Chemistry," chapter on Acetic Acid).

Commercially the following qualities are distinguished: strong charcoal (beech, oak, etc.; 1 cu. metre weighs 200–240 kilos), soft charcoal (willow, elder, poplar, walnut, etc.; 1 cu. metre weighs 135–180 kilos), and, for certain industrial uses, red charcoal, obtained by incomplete charring.

Wood charcoal contains 85–90 per cent. of carbon and has a calorific value of 6500–7000 cals.; if stored properly, it contains not more than 6–7 per cent. of moisture or 2–5 per cent. of ash.

On account of its great porosity, wood charcoal, besides as a fuel, is used to absorb gases (box charcoal, for instance, absorbs ninety times its own volume of gaseous ammonia) to decolorise syrups, and to purify liquids (to eliminate fused oil from spirit). It is also used as a reducing agent for obtaining metals from various ores, more especially from their oxides. According to the fineness of the powder (ground) and to the purity, it costs £8–£14 per ton. If purified with HF, it may cost 2*s.* 5*d.* per kilo.

In Russia, Sweden, and North America wood charcoal is still used for the production of iron. In the United States alone 400,000 tons are produced annually for this purpose, and Sweden in 1903 produced 456,000 tons, corresponding with 6 million cu. metres of wood.

The amounts of wood charcoal (tons) imported (mostly from Austria) into, and exported from Italy are as follows:

	1910	1911	1912	1913	1914	1915	1916
Importation	77,936	82,647	74,486	79,027	56,674	3,246	629
Exportation	19,066	16,920	13,960	15,124	13,617	12,357	1174

The price in normal times was £2 16*s.*–£3 4*s.* per ton.

In 1906 the output in Italy was about 500,000 tons.

ANIMAL CHARCOAL OR BONE-BLACK is another form of amorphous carbon and is obtained by heating various animal substances, especially freshly defatted and disintegrated bones (*see* p. 404 *and later:* chapter on Phosphatic Fertilisers) in closed iron or fireclay retorts; bones which have been used for the preparation of glue do not give animal charcoal. If the bones are heated in closed boilers, the charcoal obtained is richer in carbon and of higher decolorising power than when the heating is carried out in retorts which allow of the collection and utilisation of the volatile products distilling over (NH_3, CO_2, N_2O, CN, pyridine bases, ammonium sulphide, tarry products). Bone-black contains 2–8 per cent. of moisture, 75–80 per cent. of tricalcium phosphate, 6–10 per cent. of calcium carbonate, 1 per cent. of magnesium phosphate and carbonate, and 7–10 per cent. of carbon, and is sold in pieces as big as peas or beans. In certain industries, *e. g.*, those of the organic acids (tartaric and citric acids, cream of tartar, etc.), ordinary animal charcoal cannot be used, since the lime present would combine with these acids, causing loss of product or complication of the manufacture. In such cases use is made of the so-called washed bone-black, obtained by digesting the disintegrated bones in cold dilute hydrochloric acid (18 per cent.), for some days until all the mineral matter is dissolved; the remaining ossein may be expelled by distillation in retorts, the residual charcoal being extremely finely divided and having great decolorising power.

Good bone-black should not colour concentrated caustic soda solution. Its decolorising power is determined by heating standard indigo carmine solution with a definite weight of the black, filtering and titrating the indigo carmine still remaining in the solution. Bone-black has a considerable power of fixing salts, especially those of colouring matters, various solutions being hence decolorised by it; it is used in practice, therefore, particularly in sugar-works, for decolorising sugar juices, and it forms the best means of removing fusel oil from spirit (*see* Vol. II.: Alcohol), and of decolorising the most varied solutions of impure organic compounds. Owing to its special composition and to its condition of mechanical subdivision the decolorising capacity of animal charcoal is far superior to that of wood charcoal.

It becomes inactive during use and is revivified by washing with HCl, boiling with NaOH solution, thorough washing, treating with steam, drying and gentle ignition (*see* Vol. II., "Organic Chemistry," chapter on Sugar).

STATISTICS AND PRICES. When impure, in powder or lumps, it costs £12–£14 per ton, while the semi-pure product costs £40, the pure moist £70, and the chemically pure (washed with acids, etc.) £200. A good bone-black should not weigh more than 80 kilos per hectolitre.

Italy imported the following quantities (tons) of bone-black: 476 in 1908, 679 in 1909, 986 in 1910, 934 in 1912, 847 (£13,555) in 1913, 752 in 1914, 992 in 1915, and 738 (£11,815) in 1916.

France exported 2527 tons in 1913, 3373 in 1914, and 3367 in 1915, and imported 1353 tons in 1913, 783 in 1914, and 197 in 1915.

LAMP-BLACK is very finely-divided amorphous carbon obtained by the incomplete combustion (in insufficient air) of various organic substances rich in carbon. The carbon suspended in a smoky flame may be condensed on rotating iron cylinders placed over the flame and kept cold by water circulating inside them, but it is best to condense the black in cold chambers, the products depositing at different distances being kept separate, as they vary in purity and fineness.

Nowadays very good lamp-black, without brown reflection, is prepared, together with pure hydrogen, by decomposing acetylene under two or more atmospheres pressure by electric discharges in vessels at constant pressure (German Pats. 92,801 of 1886, 194,939, 203,711, 207,520, and 223,416 of 1908). This *acetylene black* contains up to 99·8 per cent. C.

Lamp-black from solids, such as resin, camphor, naphthalene, pitch, etc., is not always very pure (80 per cent. C, 1–3 per cent. ash, and the rest volatile matter), and may be freed from volatile products by calcination in closed vessels, and from mineral matter by washing with acid or alkali; 200 kilos of lamp-black are obtained from 500 kilos of pitch. Many different forms of apparatus with regulators for the air and flame are used in the preparation of lamp-black from solid, liquid, and gaseous fields.

Lamp-black obtained by the partial combustion of heavy tar oils, fats, petroleum, oil of turpentine, etc., is more pure. In the United States much lamp-black is obtained by the combustion of natural gas (Methane, *see* "Organic Chemistry").

If the lamp-black is adulterated with bone-black the ash contains phosphates, while if wood charcoal is present the ash is alkaline.

Lamp-black, which is sold as an impalpable, velvety powder or compressed in rods or cakes, is largely used for printing ink and Indian ink (a paste of lamp-black and gum compressed into cylindrical rods and dried). Acetylene black mixes well with oils, water or aqueous solutions of glue, gum, or albumin, and with the last of these is fixed in the printing of textiles. It is used in making varnishes, oil colours, blacking, crayons, goloshes, black waxed cloth, etc.

The United States produced 9200 tons of lamp-black in 1905, and Germany exported 3100 tons in 1910.

Italy imported 199 tons in 1907, 168 in 1908, 240 in 1910, 317 in 1912, 275 (£5280) in 1913, 283 in 1914, 379 in 1915, and 375 (£7500) in 1916.

France exported 896 tons in 1913, 440 in 1914, and 305 in 1915, and imported 1164 tons in 1913, 819 in 1914, and 822 in 1915.

The price varies considerably with the quality; the ordinary product is sold at £8 16*s*.–£10 8*s*. per ton, that from resin at £22–£28, that from oils, etc., at £80–£200, and contain very fine qualities at £400.

RETORT CARBON (GAS CARBON or METALLIC CARBON) also belongs to the amorphous forms of carbon. It is formed by the decomposition of the hydrocarbons evolved during the dry distillation of coal in gas-works and is found as a deposit on the internal walls of the retorts. It is very hard, has a metallic appearance, and is a good conductor of electricity and heat. It is used for the carbons in certain galvanic cells and in arc lamps and for carbon electrodes in general. It is sold in pieces or lumps at from £14 to £40 per ton.

AGGLOMERATED COAL (BRIQUETTES). These are prepared from coal or lignite dust by mixing with a small amount of binding material and exposing the mass to very high pressure in suitable moulds by means of special presses (Fig. 172).

Ordinarily dust or the smaller portions of lean coal (though not as lean as anthracite) are used, which are not suitable for the preparation of coke; 6–8 per cent. of powdered, hard coal-tar pitch is mixed with the already pulverised mass, which is then raised by means of elevators into a cylinder provided with a stirrer and heating arrangement (sometimes a small jet of steam is passed into the mixture). The pitch is thus softened and the heated mass is distributed on to a revolving plate carrying moulds into which the mixture is filled and then strongly compressed. The briquettes, stamped with the mark of the particular works, are automatically ejected from the mould.

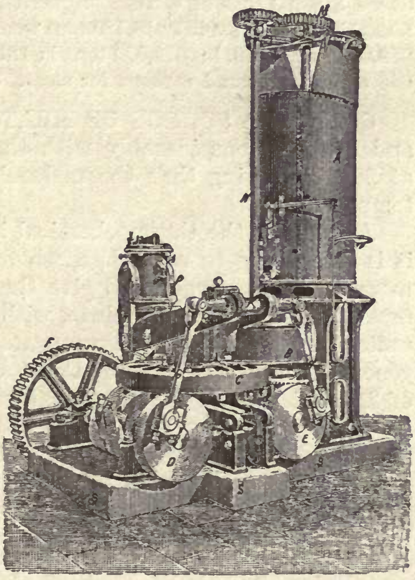


Fig. 172.

Fig. 172 does not need any further explanation. In the following figure (Fig. 173) we see another machine which is used for the production of briquettes in the shape of eggs or balls for American stoves. The hot pulverised mass is distributed between two cylinders which each carry half a mould (hemisphere) corresponding exactly, so that when the cylinders turn towards one another, the two moulds meet in the middle and form a sphere of coal with a smooth surface. In some works residues from cellulose manufacture, after evaporation, are used as a binder, with coal, a portion of the coal-tar, pitch, glue, etc., being thus saved.

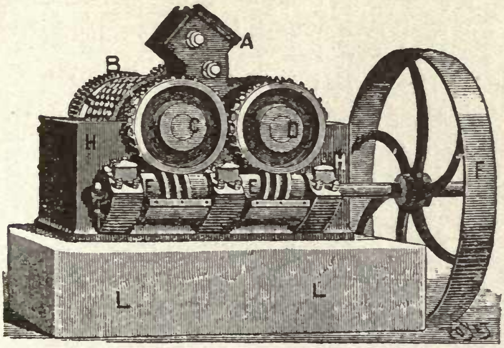


Fig. 173.

Good briquettes have a calorific power of 7700 cals. referred to the dried substance, are compact, and do not crumble in the fire. They should not contain much ash or much sulphur, and should be resistant to weathering. The pitch employed should not give more than 40 per cent. of coke and 74–90 per cent. of it should be soluble in carbon disulphide. It should have a calorific power of more than 8500 cals. and should contain less than 5 per cent. of hydrogen. In order to ascertain how much pitch has been added, the composition is extracted in a Soxhlet apparatus twice for twenty-four hours with carbon disulphide, and the extract dried for three days *in vacuo* over phosphoric acid. Good briquettes should give at least 5 per cent. of extract. They should not yield more than 8 per cent. of ash or less than 16 per cent. of volatile products.[1]

In Germany 10,476,200 tons of coal briquettes were manufactured in 1903, 13,000,000 tons in 1905, and more than 15,000,000 tons in 1907. Germany exported 940,000 tons of such briquettes in 1905, 1,090,000 tons in 1906, and 1,146,000 tons in 1909. Italy produced 829,280 tons of various briquetted fuels in 1906; 804,700 tons in 1908, valued at £948,000 (of this quantity 18,720 tons were briquettes of wood charcoal, valued at £52,000); 819,200 tons in 1911; 874,000 tons in 1912, and 969,000 in 1914. In 1907 Italy imported 945 tons of prepared carbons for electro-technical purposes and 1570 tons in 1908.

COAL AS A SOURCE OF HEAT. The specific heat of carbon is very low and increases considerably with the temperature (0·064 at $-50°$ and 0·459 at 985°), showing that the molecule is very large and complex at ordinary temperatures.

As regards the thermochemical behaviour of carbon in relation to oxygen, it is interesting to note that, whereas elements usually combine with one or more atoms of oxygen and give the maximum development of heat when the first atom of oxygen combines, with carbon this is not the case: when carbon unites directly with two oxygen atoms to give CO_2, 406 Kj. (97,000 cals.) are generated and the reaction $CO + O = CO_2$ is accompanied by the emission of 284 Kj. (67,850 cals.), so that in the fixation of the first atom of oxygen ($C + O = CO$) only 122 Kj. (29,150 cals.) are set free.

This difference between the amounts of heat developed by the first and second atoms of oxygen is probably due to the fact that the heat liberated with the first atom is not all shown by the thermometer as heat of reaction, a part being absorbed by the intermolecular work necessary to disaggregate and volatilise the complex molecule of solid carbon. When, on the other hand, CO and O unite, the CO molecules are already free, so that it may be supposed that at least 1627 Kj. (387,000 cals., *i.e.*, 67,850–29,150) are required to disaggregate the molecule of solid carbon, assuming that at least 67,850 cals. are evolved also by the first oxygen atom.[2]

The heat generated when 1 kilo of pure carbon [3] is burnt completely is 33,800 (8137 cals.) and is sufficient to melt 100 kilos of ice or to raise 80 litres of water at 0° to the boiling-point. The temperature of combustion when burnt in the air is below 1700°, whilst it is much higher when burnt in oxygen.

One h.p.-hour corresponds with 594 cals., and the efficiency of a steam-engine varies from 500 to 1000 grams of coal per h.p.-hour for a 100-h.p. engine, according to the efficiency of the condensation.

One kilo of good coal burnt under the boilers may, in practice, give 8–8½ kilos of steam and 1 h.p.-hour is obtained for 4–5 kilos of steam. In order

---

[1] One advantage of briquettes (which weigh 8–10 kilos) is that they occupy less storage space than coal in irregular lumps, this being of particular importance on ships, locomotives, etc.; the saving of space is 20 per cent. or even 30 per cent. Further, during loading, unloading, transport, firing, etc., less waste and dust (20–30 per cent. with ordinary coal, and only 5–8 per cent. with briquettes) are produced, while less passes through the fire grates.

Large briquettes remain compact under a pressure of 250–300 kilos per sq. cm., and if the mixture of coal and pitch (8 per cent.) was homogeneous, the briquettes at the bottom of a high pile are not crushed.

Machines for making large briquettes absorb 30 or more h.p. for an hourly output of 15 tons. Those for making ovoid blocks work at a lower pressure and take less power, 3–5 tons, weighing 50–200 grams each, being turned out per hour.

The specific gravity of briquettes should exceed 1·2.

[2] In these cases one speaks always of molecular calorific value, *i.e.*, the heat liberated in the combination of 12 grams of carbon with 32 grams of oxygen to form 44 grams of CO_2 (1 mol.) (406 Kj.), whereas for fuels in general, the calorific value, in small or large calories, is referred in practice to 1 gram or 1 kilo of the fuel. Thus, if 12 grams of carbon give 97,000 cals., 1 gram will give 8080 cals.; for CO (28 grams) the molecular calorific value, on burning to CO_2, is 67,850 cals., while for 1 gram of CO the heat of combustion will be 2423 cals.

[3] In the combustion of cellulose (wood), $C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O$, 17·58 Kj. (4140 cals.) are developed per kilo, and this quantity was thus required by cellulose in its formation by means of solar heat.

to determine the efficiency of boilers, these are worked for ten hours, the quantity of ash and cinders being noted, as well as the total quantity of evaporated water from the water-meter attached to the boiler.

The determination of the *calorific power* of coal, that is, the measurement of the heat developed by the complete combustion of a given weight of the coal, is of the greatest importance. In order to obtain exact and concordant results in boiler tests, the analysis should be made of a well-prepared sample, taken, for example, from various parts of a truck of coal and uniting the powder and the lumps so that about 100 kilos are taken altogether. This is then heaped up on a polished floor in the form of a square with sides about 2 metres high, the very large pieces of coal being smashed with a hammer. Diagonal and cross lines are then drawn on the heap with a piece of wood as shown, and of the eight portions so obtained  four alternate ones are removed; the 50 kilos which remain are heaped up into a similar square, the larger pieces again crushed, and the sample divided in a similar manner, so that 25 kilos are obtained, and the operations are repeated until samples of 12 and 6 kilos, and finally of 3 kilos are obtained. This sample is then taken into the laboratory, coarsely powdered, and reduced to half and a quarter as before. It is then finely powdered until the whole passes through a sieve such as is used for flour. From this sample portions are taken for the various determinations.

In contracts for the supply of coal a statement is made of the requirements with which the coal should correspond—calorific value, ash, volatile products, sulphur, moisture. The apparatus used for determining the calorific power—whether the Mahler bomb or the Lewis Thompson calorimeter—should be indicated. Directions for carrying out these determinations are given in all text-books of industrial analysis, such as Villavecchia's "Applied Analytical Chemistry," English Edition (1918), Vol. I., pp. 297 *et seq.* A good coal usually contains less than 1 per cent. S, 6 per cent. of ash, or 18 per cent. of volatile products, and should have a calorific value of 7800–8000 cals., but it should be noted that the Lewis Thompson apparatus gives lower results than the calorimetric bomb or Goutal's formula.[1]

If the calorific value of a fuel is known, it is easy to determine the amount of water which can be evaporated in a steam boiler, 100 large Calories (418 Kj.) being required to heat 1 kilo of water from 0° to 100°, and 536

---

[1] The following are the calorific values or heats of combustion of various fuels referred to 1 gram of substance and expressed in small calories, account being taken also of the heat of condensation of the water vapour (of the products of combustion) into liquid water. The values may vary somewhat with the quality:

	Cals.
Pure carbon (forming CO_2)	8,137
,, ,, (,, CO)	2,430
Perfectly dry wood	3,700
Air-dried wood	2,900
Wood charcoal	7,000
Air-dried peat	3,600
Lignite	4,000–5,500
Coal (medium)	7,500
Anthracite	8,000
Cardiff coal, No. 1	7,800–8,200
Coke from ordinary coal	7,100
Coke from lignite	5,500–6,500

	Cals.
Shales, paraffin wax, solid hydrocarbons	10,000–11,000
Ethyl alcohol	7,000
Methyl ,,	5,300
Petroleum (mixed hydrocarbons)	11,000–12,000
Heavy petroleum oils	11,000–11,500
Carbon monoxide (CO)	2,421
Water gas (equal vols. of H and CO) per cu. metre, about	3,100
Illuminating gas	4,500–5,000
Oils and fats	9,300–9,500
Methane	12,700
Ether	9,027

For certain chemical processes it may be interesting to know the heats of combustion of the following elements: Si (forming SiO_2), 7800; Mn (to MnO), 1650; Fe (to Fe_2O_3), 1740; P (to P_2O_5), 5900; Mg (to MgO), 6000; Al (to Al_2O_3), 7000 cals.

large Calories (2242 Kj.) to transform 1 kilo of water at 100° into steam at 100°.[1]

Fuels give their maximum yield of heat when combustion is complete and the carbon is completely transformed into CO_2 (1 gram of carbon thus producing 33·8 Kj. = 8080 cals.). If, on the other hand, insufficient oxygen or air is present for complete combustion, carbon monoxide (CO) will be formed instead of CO_2, and in this way less heat is developed (10·25 Kj. = 2449 cals.), and the CO is lost as it passes off with the chimney gases, whilst if sufficient oxygen were there to burn it, a further 23·5 Kj. (5631 cals.) would be produced for each gram of carbon which it contained. On the other hand, in the practical use of coal as a fuel there should be no excess of air in the furnace grate, as such excess would pass off unaltered through the chimney at a temperature of more than 300° and heat thus be conveyed uselessly into the atmosphere.[2] Practical control of the proper combustion of the coal is effected by analysing the chimney gases. If carbon monoxide is present, the draught is too weak and the quantity of air which enters the grate insufficient, whilst in absence of carbon monoxide the combustion is well regulated. The excess of free oxygen or air should not, however, exceed the usual limits, otherwise the loss mentioned above occurs. When the combustion of the coal on the hearth is properly regulated by the fireman and by a suitable chimney or mechanical draught, the chimney gases contain 12 to 14 per cent. or more of CO_2, whilst if the regulation is bad, this percentage may be 7 to 8. Further, the temperature of the gases as they reach the chimney should not exceed 300° (best 200° to 250°), since in any case these gases usually waste about 20 per cent. of the calorific value of the coal.

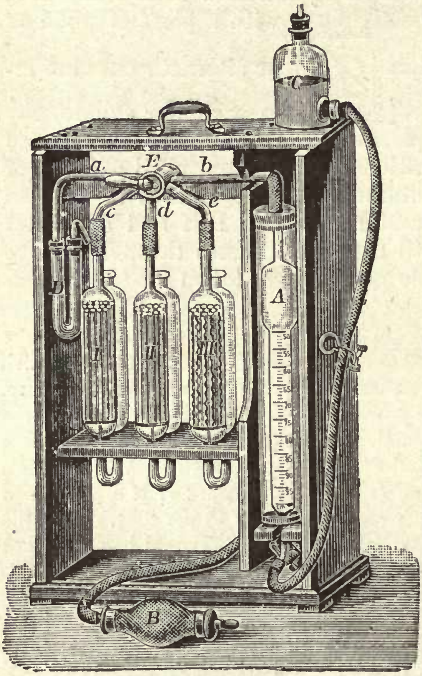


Fig. 174.

---

[1] In ordinary steam boilers without economisers, the relation between the production of steam (*a*) per sq. metre of heating surface, the consumption of coal (*b*), and the temperature of the flue gases at the bottom of the chimney (*c*) is approximately as follows:

(*a*) Kilos	12	13·5	16	18	21	25	30	35	40
(*b*) ,,	9·5	9	8	7·5	7	6·5	6·1	5·8	5·5
(*c*) Degrees	180	220	260	300	340	380	420	460	500

Preliminary heating of the water by an economiser effects a saving of 10 to 20 per cent. of fuel.

[2] On the fire-grates of steam boilers where ordinary coal is burnt, the thickness of the layer of fuel is regulated according to the size of the coal, so that the CO_2 formed in the hottest zone may not be reduced to CO in the glowing layer above, and heat be thus lost and the gases rendered too highly reducing. Usually the layer terminates just above this zone of most intense combustion (for pieces 5 to 10 cm. in diameter the layer will be about 15 cm. thick), but since the thickness of the layer of coal varies at different points an excess of air is required. In crucible furnaces and gas producers the height of this zone varies according to the velocity of the air traversing the fuel, to the size of the latter, and to the temperature desired. In crucible furnaces where a temperature of 1200° is exceeded, attention is paid only to the size of the coal and the velocity of the air; for pieces of 1 cm. side, the zone of maximum temperature is usually about 10 cm. from the bars, while for a size of 10 cm. or more (as in blast furnaces) this zone is 50 to 100 cm. up. If the temperature to be reached is below 1000°, as in water gas producers with 5 cm. lumps of coal, the zone of maximum temperature is reached at a height of 2 metres.

In analysing chimney gases a 2 to 3 inch iron tube is passed through and well sealed in the wall of the chimney at the bottom, the tube sloping slightly down towards the inside. If, however, it is not certain that no air enters the flues leading to the chimney, the gas for analysis is drawn from the space separating the flues from the boiler. A glass tube, fitted into the iron tube by a rubber bung, reaches about to the middle of the chimney and is joined outside through a rubber tube with the tube D of an *Orsat apparatus* (Fig. 174), this tube being filled with cotton wool to retain dust.

The gases to be analysed are drawn out by means of a gutta-percha valve, B, into the Orsat apparatus, and pass into the graduated burette, A, which may be emptied or filled by raising or lowering the bottle of water, C, communicating with it. The universal cock, E, is suitably turned, and the reservoir, C, raised or lowered in such a way that the gas is first passed into a vessel at the side containing a concentrated (30 per cent.) solution of potassium hydroxide, which is subdivided by small tubes of glass in order to increase the surface of contact, all the CO_2 being thus absorbed; the gas is then returned to A and its volume measured, the volume of absorbed CO_2 being given by the difference. The remaining gas is then made to enter another vessel containing an alkaline solution of pyrogallol (1 vol. of a 25 per cent. aqueous solution of pyrogallol and 5 to 6 vols. of a concentrated solution of potassium hydroxide) or yellow phosphorus, which completely absorbs the oxygen. The remaining gas is again measured in the burette, A. The gas is finally passed into a third vessel containing ammoniacal cuprous chloride solution, which absorbs the carbon monoxide, and thus the nitrogen alone finally remains. The cuprous chloride solution is obtained by dissolving 100 grams of fresh cuprous chloride in a solution of ammonium chloride (1 part to 3 of water) and adding one-third of its volume of ammonia of sp. gr. 0·910; it is kept in closed bottles containing copper turnings. The gas is made to enter and leave the graduated tube by lowering or raising the water reservoir, C.

In this way the composition of furnace gases is easily determined in a very few minutes.

There are now also forms of apparatus which automatically register the composition of chimney gases, being based on the density of these.

To obtain good evaporation in steam boilers, incrustation must be avoided by suitable correction of the water, as explained on p. 241, and the various losses of heat must be prevented as far as possible.[1]

---

[1] It is not possible to keep the hand on a naked steam pipe, but if a sheet of paper or a strip of cloth is wrapped round the pipe this can be done, and increase of the number of pieces of paper or cloth and fall of the external temperature render it the more easy. With a good insulating coating the external temperature of the pipe will be only a few degrees above the temperature of the surrounding air. Many different materials have been suggested for these insulating coatings, the choice being regulated by the coefficient of thermal conductivity, and the insulation improving as this coefficient diminishes; the lightness of the material must also be taken into account. The values of the density, d (kilos per cu. metre), and coefficient of conductivity, c, for various insulators were found by Biquart (1912) to be as follows: vegetable wool from Java (Kapok), $d = 15{\cdot}7$, $c = 0{\cdot}034$; finely divided cork, $d = 78$, $c = 0{\cdot}040$; finely divided cork agglomerated with casein, dry, $d = 148$, $c = 0{\cdot}044$; wood charcoal in flakes, $d = 184$, $c = 0{\cdot}045$; corrugated card, $c = 0{\cdot}052$; white asbestos fibre, $d = 57$, $c = 0{\cdot}054$; corrugated asbestos card, $c = 0{\cdot}072$; cork agglomerated with moist casein, $d = 280$, $c = 0{\cdot}088$; cork agglomerated with pitch, moist, $d = 310$, $c = 0{\cdot}076$; compressed asbestos, $d = 1240$, $c = 0{\cdot}220$; compressed cellulose, $d = 1425$, $c = 0{\cdot}210$; asbestos and gypsum bricks, $d = 1143$, $c = 0{\cdot}350$; slag bricks, $d = 1400$, $c = 0{\cdot}400$; talc, $d = 1470$, $c = 0{\cdot}430$.

The following practical results were obtained with various insulators applied to a steam pipe in a coating 40 mm. thick. Martinite antithermic felt (made of spongy blast-furnace slag, a little asbestos, etc.), $d = 300$, c (*i. e.*, increase of temperature in the insulator for each degree of difference between the inside and outside) $= 0{\cdot}08$, K (*i. e.*, calories lost by the insulator per sq. metre of external surface per hour per degree difference between inside of the pipe and the surrounding air) $= 1{\cdot}70$, V (kilos of steam condensed by the insulator per sq. metre per hour) $= 1{\cdot}115$; Lucy insulator, $d = 366$, $c = 0{\cdot}10$, $K = 2$, $V = 1{\cdot}260$; Magnesia covering, $d = 240$, $c = 0{\cdot}12$, $K = 2{\cdot}44$, $V = 2{\cdot}300$; Silicate cotton (spongy blast-furnace slag), $d = 400$, $c = 0{\cdot}09$, $K = 2{\cdot}68$, $V = 2{\cdot}515$; Kieselguhr, $d = 361$, $c = 0{\cdot}128$, $K = 2{\cdot}15$, $V = 2{\cdot}500$; mica paste, $d = 670$, $c = 0{\cdot}139$, $K = 2{\cdot}85$, $V = 4{\cdot}570$; baked Kieselguhr bricks, $d = 400$, $c = 0{\cdot}168$, $K = 2{\cdot}95$, $V = 3{\cdot}850$; asbestos fibre, $d = 360$, $c = 0{\cdot}179$, $K = 3$, $V = 3$; woven asbestos, $d = 570$, $c = 0{\cdot}182$, $K = 3{\cdot}12$, $V = 3{\cdot}20$; asbestos in cord or paste, $d = 585$, $c = 0{\cdot}193$, $K = 3{\cdot}20$, $V = 3{\cdot}530$. The tests were made on an iron pipe through which steam at 14 atmospheres (temperature = 195°) was passed, the temperature of the surrounding air being 34° (hence temperature difference between inside and outside = 160°); without lagging, $K = 34$ and $V = 4{\cdot}560$. The last figures show the enormous waste of heat and hence of coal

FLAMELESS OR SURFACE COMBUSTION.[1] As early as 1817 Davy showed that a red-hot platinum wire, when immersed in a mixture of combustible gas with a little air,

---

when steam pipes are not covered. For calculating the losses of heat, the following data are useful: Thermal conductivity: Iron, 1; copper, 6·1; lead, 0·7; glass, 0·0096; water, 0·009; vulcanite, 0·00156; air, 0·0003. Radiation of heat in calories per second per sq. metre of surface: Ag, 0·13 to 0·23; Cu, 0·16; Zn, 0·24; Sn, 0·715; Pb, 0·65; bright iron, 0·45; black sheet iron, 2·77; oxidised sheet, 3·36; cast-iron, 3·17 to 3·36; gypsum, 3·60; brickwork, 3·68; wood, 3·60; oil, 7·24; oil paint, 3·71.

[1] **Nature of Flame.** Flame is generated by the incandescence of the gaseous particles resulting from the chemical reaction between the oxygen of the air and solid, liquid, or gaseous substances, accompanied by considerable evolution of heat and rise of temperature. With organic substances, which contain carbon and hydrogen (illuminating gas, for instance, contains much H, CH_4, CO, etc.), the atmospheric oxygen transforms the hydrogen into water and the carbon into CO and CO_2 with liberation of much heat.

A flame becomes luminous when certain hydrocarbons containing much carbon decompose with liberation of carbon particles through insufficiency of oxygen; these particles become incandescent and very luminous. Thus, on heating, ethylene readily separates carbon: $C_2H_4 = CH_4 + C$ and so does acetylene: $2C_2H_2 = CH_4 + 3C$. In Bunsen burners, such as are used in laboratories, a luminous or colourless flame may be obtained at will by allowing more or less air to enter the tube which carried the gases to the flame.

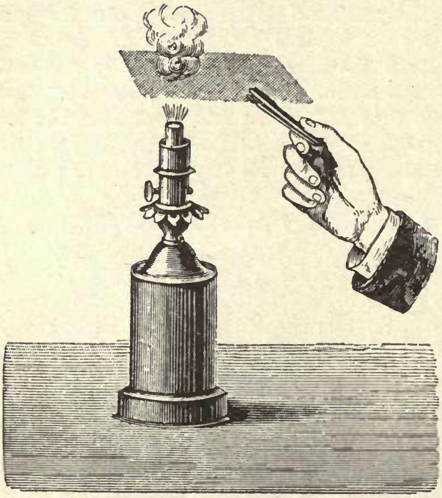


FIG. 175.

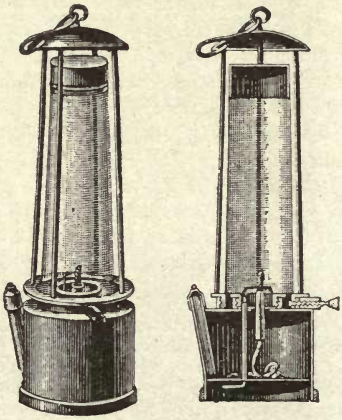


FIG. 176.

A flame may be oxidising or reducing according to the excess or deficiency of air or oxygen mixed with the gas during combustion, and this property of flames is of great practical importance through the application which is made of it in various industries, in which either an oxidising or a reducing flame may be required according to the circumstances. In the colourless flame of the Bunsen burner the internal nucleus of the flame, where the gas is abundant and there is a deficiency of air, has a reducing action, whilst the external portion, and especially the point of the flame, is of an oxidising character. We have also seen that, under different circumstances, many combustible substances may act as supporters of combustion, for example, hydrogen, chlorine, ammonia, etc.

If a jet of lighting gas is projected on to a metallic gauze (Fig. 175) the gas may be lit above the gauze without the flame passing through it. Thus a flame may be isolated by means of a piece of metallic gauze from the gas supply by which it is fed, because the gauze is such a good conductor of heat that the heat produced by contact with the flame is rapidly dispersed to every side, so that the temperature of the gauze is maintained below that which is necessary to ignite the inflammable gas on the other side of it.

This property was utilised by Davy in his miners' safety lamp (Fig. 176), which consists of a simple oil-lamp the flame of which is completely surrounded by a metallic net. If this lighted lamp is introduced into an atmosphere full of inflammable gas, the gas penetrates to the interior of the metallic gauze and is ignited, but the flame cannot communicate with the outside. These lamps are, therefore, employed by miners, because when explosive gases are formed in the mine, the lamps may be used for illumination without the risk of explosion.

Flames of oil, candles, paraffin, and alcohol are extinguished in air containing 15 per cent. of carbon dioxide, whilst a gas flame resists amounts of carbon dioxide up to 33 per cent., and a hydrogen flame will burn in an atmosphere containing 58 per cent. of CO_2, that is, in only 8·8 per cent. of oxygen. This fact may also be utilised in the construction of miners' safety remains glowing, *i. e.*, it causes gradual flameless combustion until the whole of the oxygen present is consumed. In 1823 Dulong and Thénard, and independently Döbereiner, showed that many red-hot substances (best if powdered) are able to induce combustion of gases without flame. Platinum sponge is active even at the ordinary temperature, silver and gold at 150° to 250°, and porcelain, pumice, glass, etc., at about 350°. W. Henry (1825) and Graham (1829) found that, when a sphere of platinum is introduced into a mixture of $2H_2 + O_2$ with ethylene, only the hydrogen and oxygen combine, the ethylene remaining unchanged. In 1834–1835 De la Rive explained the phenomenon as due to rapid oxidations and reductions of the catalyst, while Faraday held that the function of the solid body and of the catalyst consists in condensing at its surface much combustible gas and much oxygen, just as if these gases near the solid surface were exposed to a high pressure.

J. J. Thomson and, later, Kinzbaunner attempted to explain the phenomenon by the electron theory.

In 1887 Fletcher directed a current of air and gas against a red-hot ball of iron wire and then blew out the flame, but kept the gas current flowing; by this means the gas was made to burn without flame and the iron wire kept red-hot.

The practical application of flameless combustion, after the studies and experiments of Professor Bone of the University of Leeds, published in March 1911, and those of Schnabel, published in September 1912, is based on the following considerations:

Methane combines more energetically with oxygen than hydrogen does (the velocities are in the proportion 20 : 1), but in contact with, or in presence of hot surfaces (at 500°) this rule becomes reversed.

Water vapour has considerable influence on the combustion of CO with oxygen. In 1881 Dixon showed that, if both gases are dry, even electric sparks will not cause combustion, but a trace of moisture is sufficient to cause union in this detonating mixture ($2CO + O_2$). In presence of hot surfaces (pieces of porcelain at 500°), however, the velocity of combustion of this mixture is doubled if no water is present; this result is due to the ionising action of the hot surface on the combustible gases.

It has been shown also that, whereas at relatively low temperatures there are marked differences between the actions of different catalysts, these actions become almost equal at high temperatures (white-red heat), although in certain chemical reactions too high temperatures dissociate the substance formed (*e. g.*, $SO_3 \longrightarrow SO_2 + O$).

If a mixture of illuminating gas and air is passed through the pores of a porous plate of refractory material, already heated, the combustion of the gas takes place on the opposite surface of the plate and is complete and gives the maximum temperature when the theoretical amount of air is used, since then the velocity of reaction or combustion is at its maximum. Thus, if a mixture of hydrogen and oxygen (or air) is ignited the greatest detonation, *i. e.*, the maximum velocity of reaction, is obtained when the quantity of oxygen present corresponds with the theoretical amount for complete combustion of the hydrogen (in a mixture of $2H_2 + O_2$, the ignition or explosion is

---

lamps, a hydrogen flame being made to burn in them simultaneously with the oil flame. When the oil flame is extinguished it is a sign of danger to the miner, because in 15 per cent. of CO_2 he would quickly be suffocated. When the miner in returning arrives at a point where the air is pure, the hydrogen which had continued to burn lights the oil flame again.

The temperature of a flame in general is lower than that deduced from theoretical calculations. Thus, in the flame of hydrogen burning in oxygen, the temperature is calculated as follows: A gaseous mixture formed from 16 grams of oxygen and 2 grams of hydrogen develops 68,400 cals. on burning and forms 18 grams of water vapour, and since the specific heat at constant pressure of water vapour is 0·48, for a rise of temperature of 1° of 1 gram of water vapour, 0·48 cal. is required, so that 68,400 cals. should heat 18 grams of water vapour to a temperature of $\frac{68,400}{18 \times 0{\cdot}48} = 7909°$; in practice, however, exact measurement shows that the actual temperature of the oxy-hydrogen flame is little more than 2500°.

This abnormality is explained by the fact that the specific heat of water vapour at very high temperatures increases, but more especially because towards 1300° the water vapour which is formed commences to dissociate into its components, H_2 and O, and then absorbs as much heat as is developed during its formation, so that the temperature of the flame cannot rise to 7909°, as was calculated theoretically. When carbon burns vigorously in air, a temperature of about 1700° is reached, but when it burns in an atmosphere of oxygen, the temperature is much higher. The temperature of the electric arc as measured directly with pyrometers is 3690° to 3720°, but some authors hold that the temperature reaches 5730°.

porpagated at a velocity of 2841 metres per second, whilst when the proportions are varied, the velocity or the detonation diminishes, as explained on p. 136). Flameless or surface combustion occurs, not during the passage of the gas through the partition, but on the hot wall opposite to that entered by the cold gas and, as the velocity of combustion is greater than that of arrival of the gas through the porous partition, there is no time for the gas to form a flame, since as it arrives it is completely burnt, perhaps by a catalytic action of the hot porous surface.

If, for instance, a mixture of 12 litres of air with 2 litres of illuminating gas is passed per hour per sq. cm. through a plate with 40 per cent. of porosity (*i. e.*, 40 per cent. of empty space per 100 of total volume of the plate), the linear velocity will be 0·10 metre per second, which is about one-third of the velocity of combustion of this gaseous mixture.

The gases are forced through the porous disc under a pressure of from one-third to one-half of an atmosphere, and while one face of the disc is incandescent the opposite face is almost cold; the temperature of the incandescent surface may be varied by altering the pressure of the gas. When illuminating gas is burnt with air, the free incandescent surface may reach a temperature of 850°, which is maintained even if this surface is immersed in an atmosphere of carbon dioxide.

This system of combustion is applicable to any combustible gas having a calorific value such as to bring to redness the surface of the porous diaphragm, and if the temperature on the hot surface of the plate exceeds 685°, the combustion is not propagated through the thickness of the diaphragm.

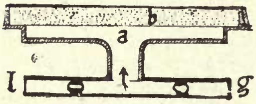


FIG. 177.

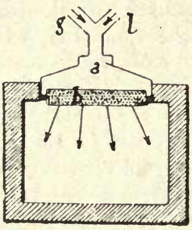


FIG. 178.

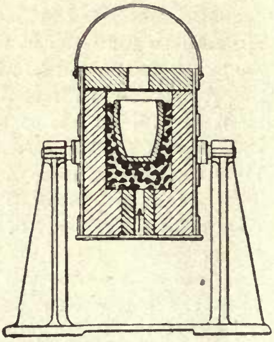


FIG. 179.

To obtain temperatures above 850° the porous plate is replaced by a heap of fragments of refractory material. From the lower part of the heap the combustible gas above is first passed, this being ignited with a flame at the surface of the heap. A current of air is then passed together with the gas from the bottom, and is so regulated that the flame is not luminous, but slightly bluish, like a Bunsen flame; the combustion is then propagated throughout the whole heap to the very bottom, and the fragments are thus rapidly heated to redness, and the whole mass becomes incandescent. The velocity of combustion is then maintained high at the surface of the fragments without arrival of air from the bottom of the heap, that penetrating from the layer of air surrounding the incandescent heap being sufficient; in such case, however, the velocity of arrival of the gas should be greater than that of combustion, in order that the combustion may take place in all the free spaces of the heap of fragments. In this way with blast-furnace gases (*see* chapter on Iron) a temperature of 1000° can be obtained, with Mond gas 1500°, with illuminating gas 1900°, and with air gas 1900°, if fed with cold air; if the heat is recovered to heat the feed air, still higher temperatures are attainable.

The simplest demonstration apparatus used by Bone consists of a moderately porous disc, *b*, of refractory material (Fig. 177), 25 mm. thick (formed by making a paste of clay particles 1·6 to 2·3 mm. in diameter, powdered felspar, and water, allowing to dry in the air and heating gradually in a furnace), supported by iron framework forming the chamber *a*, into which the gas passes by means of the tube *g*, to be ignited at the outer surface of *b*, where it burns with a bluish flame. If, now, air at a suitable pressure is also passed in through the tube *l*, the flame gradually shortens and finally disappears, but the surface of the diaphragm remains red-hot, since the combustion of the gas continues without flame when only the theoretical amount of air is mixed with the gas; the hot disc may be used to heat articles, either by contact or by radiation—by arranging the disc in the upper part of a heating chamber, as shown in Fig. 178. For heating crucibles or muffles, use is made of the device shown in Figs. 179 and 180, the crucible or muffle being surrounded with pieces of refractory material through which the gas and air are passed from the bottom; the gas mixture is ignited at the upper orifice. With large furnaces the refractory material is arranged in channels on the sides of the basin; the gaseous mixture is led in by two pipes, and the heat is reflected by the arch of the furnace on to the whole surface of the basin. The hot gases issue at the top of the furnace and pass through underground flues, then through a chamber containing radiator tubes, which heat the air used for the combustion of the gas. To melt large quantities of metal use may be made of iron vessels in which are arranged one or more iron pipes, about 8 cm. in diameter, filled with fragments of refractory material; into these pipes the gas and air are passed by means of a lateral pipe reaching to the bottom, as shown in Fig. 181. In such an apparatus, used for the fusion of 500 kilos of lead per hour, the thermal yield obtained was 68 per cent.

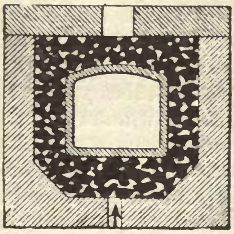


FIG. 180.

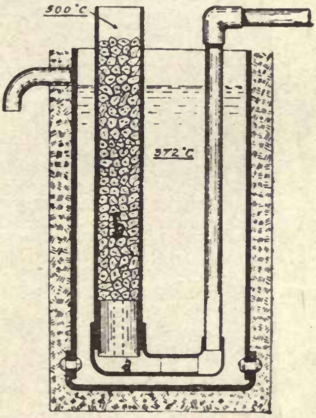


FIG. 181.

Of great importance is the application of flameless combustion to steam boilers of even large dimensions, *e.g.*, that shown in Figs. 182, 183, 184, and 185, which has the form of a drum, 3 metres in diameter and 1·2 metre wide. In the lower half are arranged 114 horizontal tubes, *b*, of external diameter 87 mm. and bore 75 mm. The upper half of the boiler is traversed by sixteen stays, which hold fixed the two opposite end-plates. The tubes *b* are filled with fragments of refractory material 1 to 2 cm. in diameter, and the first 10 cm. of each tube, towards the gas-distributing chamber, 2, carries a refractory plug with an aperture of 9 mm. for the ignition of the gaseous mixture. The collecting chamber, *c*, leads the hot combusted gases through the tube *d* to the economiser, *e*, consisting of a small drum 1·47 metre in diameter and 0·47 metre wide, traversed by

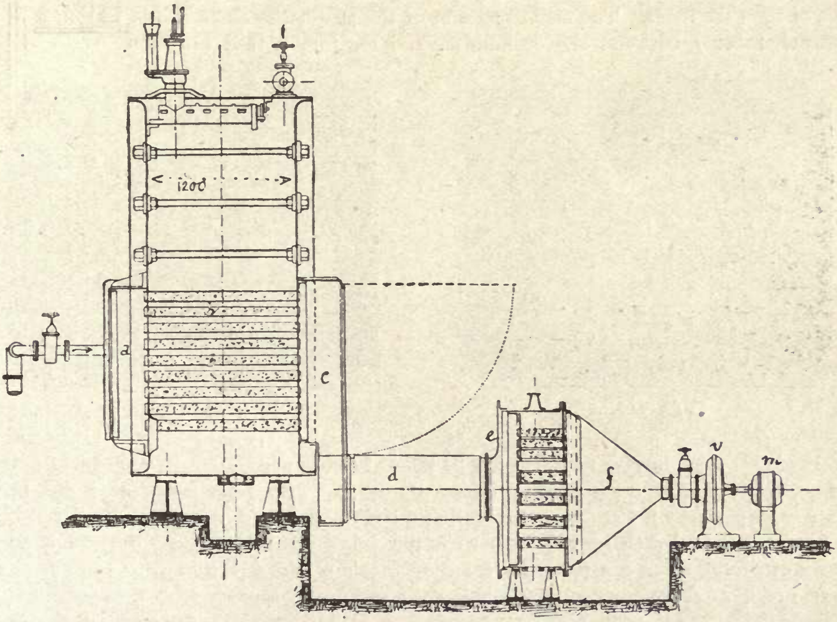


FIG. 182.

a hundred tubes filled with fragments of refractory material. The heating surface of the boiler is 31 sq. metres and that of the economiser 10·6 sq. metres. The gases are drawn in by means of a fan, *v*, worked by a motor, *m*, and a number of the combustion tubes, *b*, can be closed completely by plugs, according to the greater or less amount of steam required. At the beginning the mixed gases are ignited in the chamber *c* by suitable igniters, and as the tubes gradually become heated the flame withdraws and then disappears, combustion continuing and keeping the tubes red-hot. The temperature is distributed throughout each tube according to the diagram reproduced in Fig. 186. The combustion occurs in the first 100 to 150 mm. of the tube, and in this zone the temperature rises to 1400° or 1600° along a central portion 10 to 15 mm. in diameter and 40 mm. in length. In the whole of the rest of the tube the fragments of refractory material serve to retard the velocity of the hot, burnt gases and to store and radiate the heat homogeneously towards the walls of the tubes which heat the water of the boiler. The temperature falls rapidly, however, towards the ends of the tubes, and the gases issue at about 170°. The refractory plug serves the purpose of removing the combustion a little from the point where the tube is inserted in the metal, and the central orifice of the plug directs the gas along the axis of the tube without heating the walls of the tube itself. The mean pressure of the gas in the channel *d* is 430 mm., while in the chamber *f* between the economiser and the fan, *v*, it is 515 mm. With certain boilers of this type, having an output of 50 kilos of steam per hour per sq. metre of heating surface, a yield of 92·5 per cent. is obtained, the loss of 7·5 per cent. being due to the chimney (2 per cent.), fan (2·5 per cent.), and radiation (3 per cent.).[1]

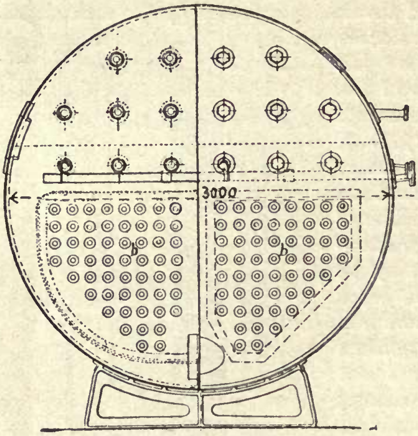


FIG. 183.

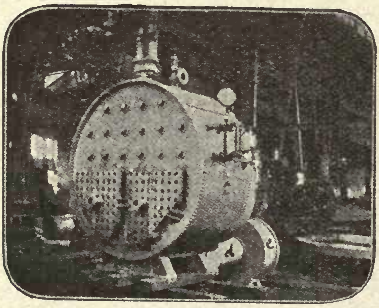


FIG. 184.

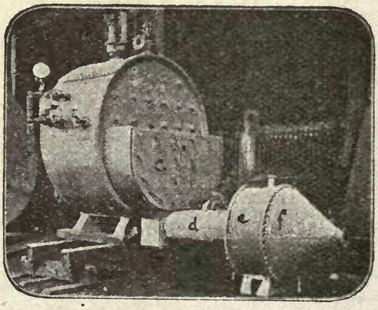


FIG. 185.

In a small boiler (Figs. 187, 188) with ten tubes similar to those described, 30 cu. metres of illuminating gas (calorific value 5000 cals.), mixed with 170 to 180 cu. metres of air, are burned per hour. In the boiler the steam has a pressure of 8 atmos., and the

---

[1] The following data refer to a five-hour test made on a Bone boiler, using coke-furnace gases containing 2·5 per cent. CO_2, 3·7 O, 6·5 CO, 23 CH_4, 48 H, and 11·3 N, and having a calorific value of 4630 cals. Gas consumed = 1250 cu. metres at 17·7°, and (= 1137 cu. metres at 0°) at a pressure of 78·8 mm. of water at the meter and 15·3 mm. in the chamber *a*; pressure of steam in the boiler, 6·86 atmospheres; depression of the gases in the channel *d* = 266 mm. of water and temperature 188°; depression in the chamber *f* = 286 mm. and temperature 90°; rise of temperature of the water in the economiser, 17·5° to 54·9°; total calories of the gas consumed, 5,268,858; total heat utilised by the steam, 4,940,895; saturated steam per sq. metre per hour = 44 kilos; consumption of energy by the fan, 5·49 kilowatts (= 549 kilos of steam); nett final efficiency, 90·4 per cent.

gas issues from the tubes at 230° and from the economiser at 95°. The burnt gases contain 10·6 per cent. CO_2 and 1·6 per cent. O and no trace of CO, H, or CH_4, so that an excess of only 0·5 per cent. of oxygen suffices to obtain complete combustion.

A large boiler has worked since November 1911 in the metallurgical works of the Skinningrove Iron-works, Cleveland (Yorkshire), and has produced 2500 kilos of steam per hour.

The thermal balance for the fusion of 533·4 kilos of lead per hour is as follows: consumption of illuminating gas giving 4975 cals. per cu. metre, 2831 cu. metres per hour; the lead was introduced at 15° and flowed away at 372°; the burnt gases on leaving the mouth of the tube had a temperature of 500°. Taking into account the specific heat of lead and the heat necessary to melt the lead and raise its temperature 357°, 18·14 Cals. are required per kilo of lead fused, so that 533·4 kilos require 9674 Cals. The heat furnished by 2831 cu. metres of gas is 14,084 Cals., the calorific efficiency being 68·7 per cent.; if, however, the burnt gases at 500° are utilised otherwise, the yield may exceed 85% to 90%.

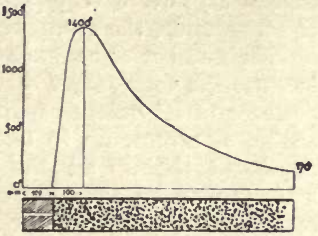


FIG. 186.

From various experimental results, F. Krull (1913) draws up the following rather optimistic summary of the advantages of surface combustion, both with Schnabel-Bone boilers and Schnabel-Bone hearths: heat efficiency, 93 per cent.; evaporating power, 100 to 130 kilos per cu. metre of heated surface per hour (*i. e.*, double or treble that of ordinary boilers); easy adjustment to variations of load; simple and economic construction; almost automatic working; elimination of the ordinary costly and cumbrous brickwork of the boilers and chimney; minimal wear and diminished incrustation of the boilers; less space required in comparison with the ordinary bulky steam boilers. Temperatures up to 2000° may be reached and combustion takes place without an excess of air (as is necessary in all other ordinary systems of combustion).

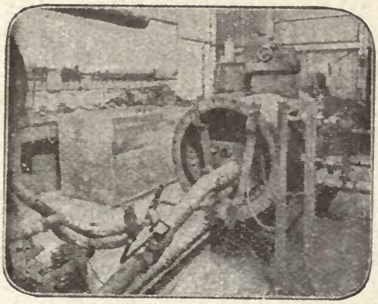


FIG. 187.

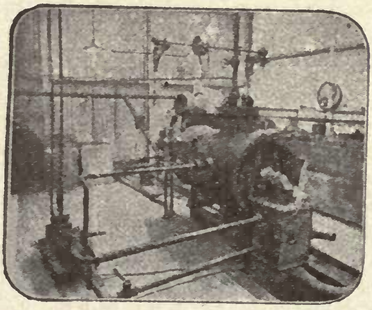


FIG. 188.

It is possible by this system to obtain high efficiency with inferior gaseous fuels, such as blast-furnace gases, and even the exhaust and incompletely burnt gases of gas and heavy oil engines and producer gas from lignite and peat.

The combustible gas must be freed from dust or ashes, since, if the active surface of the refractory material becomes covered with dust, its action almost or quite ceases instantaneously. It is necessary also to make frequent analyses of the gas-air mixture, in order to ensure that it has the correct composition. In steam boilers no incrustation is formed, since the very high temperature inside the boiler keeps the water in continuous and tumultuous movement, which prevents the formation of compact incrustation, so that the solid matter separated remains powdery.

CARBON COMPOUNDS

At the ordinary temperature carbon is one of the chemically more indifferent elements, and in the cold it combines with fluorine only. It does not combine with the other halogens, even on heating. At high temperatures, however, when the carbon molecules are less complex, it combines with various elements, and at the temperature of the electric arc it unites directly with hydrogen, forming acetylene, C_2H_2. In the electric furnace it unites with silicon at 1400° and forms *carborundum* CSi (*see below*), and it also combines at this temperature with various metals (Ca, Ba, Mg, etc.), forming numerous carbides. With oxygen it forms two oxides, CO and CO_2, on heating, and with sulphur vapour it forms carbon disulphide, CS_2. When combined, especially with hydrogen, carbon acquires a very great capacity for reaction, and then forms thousands of compounds, the study of which is the sphere of organic chemistry.

The number of compounds which carbon can form is theoretically infinite, because the tetravalent carbon atom has the property of saturating one, two, or three of its valencies with other carbon atoms, forming more or less long chains of atoms, up to twenty and thirty atoms long, in direct, branching, or closed chains; all the valencies which remain free are saturated by hydrogen or by elements of other groups, as is explained at length in the second volume of this work (" Organic Chemistry ").

The halogen compounds of carbon are very numerous and are ordinarily studied together with organic chemistry. One of great industrial importance, namely, the tetrachloride, will, however, be considered here.

CARBON TETRACHLORIDE: CCl_4

This compound is a colourless liquid of similar odour to chloroform, has a specific gravity of 1·629, boils at 77°, and solidifies in crystals at − 24°; its specific heat is 0·2 and its heat of evaporation is 51 cals. (per 100 litres 9800 Cals. as for benzine). It dissolves paraffin wax and various resins (but not copal), especially in presence of 10 to 20 per cent. of alcohol; it is an excellent solvent for fats, even if the substance is slightly moist, in which case the fat would not be extracted by benzine, and it has the advantage of being non-inflammable; when mixed with 10 to 20 per cent. of alcohol it is also a good solvent for resins; when mixed with sulphoricinoleic acid it dissolves in water.

It is prepared by passing dry chlorine through carbon disulphide (CS_2) containing a little iodine in solution (or in which a catalyst formed of asbestos impregnated with $MgCl_2$ is suspended); this facilitates the chlorination: $CS_2 + 6Cl = CCl_4 + S_2Cl_2$.

On distillation CCl_4 passes over, and sulphur chloride, S_2Cl_2, remains behind.

In presence of a little powdered iron S_2Cl_2 is also transformed into CCl_4, thus: $CS_2 + 2S_2Cl_2 = CCl_4 + 6S$, and the latter is re-utilised for the preparation of CS_2.

The tetrachloride is purified by washing it with a solution of sodium hydroxide and then rectifying it over a solution of calcium hypochlorite containing 6 per cent. of Cl.

It has been found that CCl_4 attacks the metals, especially in presence of water, through formation of HCl, and its high price formerly prevented it from being used industrially on a large scale as a solvent to replace benzine, etc. It is to-day, however, placed on the market in the pure state at a price of £24 to £26 per ton, and under these circumstances it is already used for degreasing wool, fabrics, bone, etc., but lead-lined or tinned apparatus with nickel-plated cocks and valves has to be used. The vapours of CCl_4 are not more narcotic than those of benzine.

CCl_4 also renders other solvents almost non-inflammable when added to them in the proportion of 50 to 80 per cent. During the last few years the manufacture of chlorinated derivatives of acetylene (chloro-derivatives of ethylene and ethane: $C_2H_2Cl_2$, dieline; C_2HCl_3, trieline; C_2HCl_5, pentaline; etc.) has been started in the Usines électriques de la Lonza at Geneva; these products are non-inflammable liquids and do not attack metals.

In Italy in 1907 50 tons of carbon tetrachloride were produced at £24 per ton, and although it has not yet been widely used industrially on account of its high price and of the fact that it corrodes the metals, lead-lined and tinned vessels resist it sufficiently well, and nickel resists even moist CCl_4 excellently. In 1908 the production dropped to 8 tons, but rose to 81 tons (£2754) in 1914 and 119 tons (£4046) in 1915.

CARBON TETRA-IODIDE, CI_4, forms ruby-red octahedra and contains 97·6 per cent. of iodine. It may be obtained by the action of a solution of aluminium iodide in carbon disulphide on CCl_4; or from calcium (or boron or lithium) iodide and CCl_4 in a closed tube at 75° to 80°; or from iodoform and hypochlorite in presence of alkali at 45°. It is soluble in organic solvents, and would probably be of great medicinal use if it did not decompose so readily in the air. With hydrogen it gives iodoform at 100°, and hydrogen iodide, methylene iodide, and methyl iodide at 160°, and with potash it yields methane. With silver nitrate it yields quantitatively $CO + CO_2$ and silver iodide and iodate.

CARBON DIOXIDE : CO_2 (CARBONIC ANHYDRIDE)

This gas is also incorrectly called *carbonic acid.* It is a gas which is always found in the free state in the atmosphere in the proportion of 4 litres per 10,000 litres. Expired air (the product of animal respiration) contains 4 or 5 per cent.; thus the air of rooms or of places in which many people congregate rapidly becomes unsuitable for respiration through the diminution of the oxygen and increase of CO_2, for a man breathes in about 700 grams of oxygen daily and expires about 900 grams of CO_2 in the same period. Natural sources of carbon dioxide are found in volcanic neighbourhoods; at Bohl in the Rhine Province 300 kilos of carbon dioxide are evolved every twenty-four hours; large quantities of CO_2 are found at Pyrmont; in the Grotto of Dogs at Pozzuoli near Naples, the gas of which contains 67 to 71 per cent. of CO_2, about 6 per cent. of oxygen, and 25 per cent. of nitrogen; at Pergine (Tuscany) there is an abundant source of CO_2, which is utilised industrially by the firm of Cesare Pegna and Sons of Florence. It is found in all active volcanoes, especially in those of South America; at Sondra in Thuringia there is a spring which yields 1000 cu. metres of pure CO_2 (99 per cent.) per hour. If the carbon dioxide in the earth's crust is present under pressure in contact with water the latter absorbs very large quantities and rises in the form of mineral springs as acid mineral water. This water often dissolves iron during its course and becomes ferruginous. In the form of calcium and magnesium carbonates carbon dioxide forms entire mountain ranges.

When carbon, coal, or organic substances in general are burned completely, in presence of a sufficient quantity of air, CO_2 is always formed. Also, when calcium or magnesium carbonate is heated to redness CO_2 is formed abundantly : $CO_3Ca = CaO + CO_2$, whilst the alkaline carbonates are not decomposed by such treatment. When carbonates are treated with dilute hydrochloric acid, the whole of the CO_2 which they contain is evolved :

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

In the laboratory a regular supply of carbon dioxide is obtained by the action of dilute hydrochloric acid on lumps of marble, the same apparatus being used as for hydrogen (*see* p. 139).

Carbon dioxide is formed abundantly in all fermentation processes, especially in those of sugar solutions (such as grape must, wort, etc.), and is utilised industrially (*see* Vol. II., " Organic Chemistry ").

PROPERTIES. Carbon dioxide is a colourless gas with an acid smell and taste. Its specific gravity is 1·529 (air = 1) and 1 litre at 0° weighs 1·976 grams; being so heavy it may be collected by displacement of air and may be poured from one vessel to another just as though it were a liquid.

A very striking demonstration of the great density of CO_2 may be based on the different velocities of diffusion of gases differing greatly in the size of their molecules (p. 40). For this purpose use may be made of the Ansell apparatus with an electric bell, which also serves as an automatic indicator in mines, cellars, and in all cases in which the air may become mixed with a heavier or lighter gas. Fig. 189 shows one form which Ansell's apparatus may take. A glass funnel with a long neck bent into a U-tube is filled with mercury up to the level, *d;* the funnel is closed by a porous disc of plaster or unglazed earthenware. The tube *b* is closed by a cork stopper carrying an iron or platinum wire which does not dip into the mercury and is connected with one of the poles of a battery, this communicating with an electric bell; a platinum wire sealed into the U-tube at *d* is united with the same pole of the battery, whilst another wire sealed into the U-tube at *c* is connected with the electric bell. Air is present in the funnel, *a*, and when this is surrounded outside by an atmosphere containing CO_2, the mercury rises in the tube and comes into contact with the platinum wire in *d*, the current then passing and the bell ringing. By regulating the height of the mercury or of the metallic contact, the apparatus may be arranged to ring with any definite percentage of CO_2. If, on the other hand, the funnel is surrounded by an atmosphere of a gas lighter than air, such as lighting gas, hydrogen, firedamp, etc., the mercury is forced down and rises in the other limb of the tube until it comes into contact with the platinum point, *b;* contact is then again made and the bell rings.

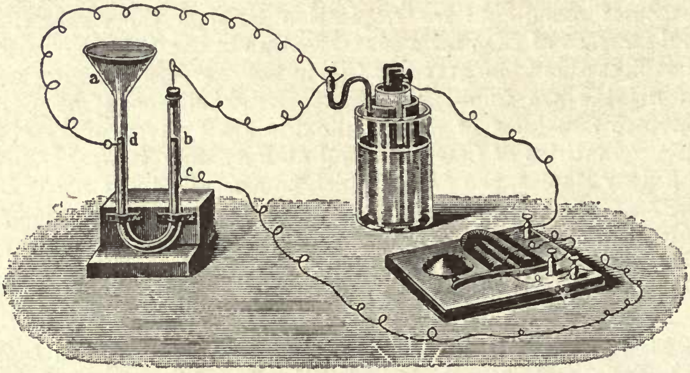


FIG. 189.

The critical temperature of CO_2 gas is 30·9° (critical pressure 77 atmospheres; *see* p. 28) and above this temperature it cannot be liquefied whatever the pressure may be. When liquefied it boils at — 78·2°, with such great absorption of heat that the remaining CO_2 solidifies. Solid carbon dioxide forms a white snow-like mass which melts at — 57° under a pressure of 5 atmospheres, whilst if the pressure is less it gasifies without melting, because at ordinary pressures the boiling-point is lower than the melting-point.

These remarks apply also to all substances which at their melting-points have vapour pressures superior to the atmospheric pressure. Thus, the vapour pressure of melting (and liquid) CO_2 is 3·5 atmospheres, and if the pressure is less than this, then it passes from the solid directly into the gaseous state (sublimes), as happens with As_2O_3, calomel (HgCl), and camphor, which can be obtained liquid only by melting them in sealed tubes under pressure. On the other hand, solid bodies which liquefy at the ordinary pressure, such as iodine, mercuric chloride, etc., may be sublimed directly if at the melting-point the pressure is diminished below that of an atmosphere. Carnelley called the pressure below which a solid body can no longer be liquefied, but passes directly into the gaseous state, the *critical pressure of solids.* For ice the critical pressure is 4·6 mm., and for all other substances it indicates the vapour pressure at the melting-point.

Faraday had already liquefied CO_2 in 1823. The experiment was repeated by Thilorier in 1834, and still later Natterer obtained liquid CO_2 easily and in abundance by means of special apparatus using high pressures. In order to liquefy it at the ordinary temperature of 20°, a pressure of 50 atmospheres is required. It then forms a colourless, very mobile liquid which has a specific gravity of 0·726 at 22°, and of 0·91 at $-1·6°$; it has thus a much greater coefficient of dilatation than the gas, and this is also true for all substances which are liquefied under strong pressure. When solid carbon dioxide is mixed with a little ether a paste is formed which, at reduced pressure, produces a cooling down to $-140°$.

One volume of water at 14° dissolves an equal volume of CO_2; at 2 atmospheres pressure it dissolves 2 vols., at 3 atmospheres 3 vols., and also at higher pressures Henry's law is followed exactly; when the pressure is diminished the dissolved gas is liberated.

Carbon dioxide does not burn because it is itself the product of the complete combustion of carbon, and on account of its great stability it does not maintain combustion or animal respiration. Its molecule is not dissociated even when heated to 2000°, and at 2367° the degree of dissociation is only 26·6 per cent., and at 2843°, 63·4 per cent. Magnesium, however, when heated to redness, continues to burn in an atmosphere of CO_2, because its chemical energy is so great that it is able to abstract the oxygen, with separation of carbon: $CO_2 + Mg_2 = 2MgO + C$; potassium, sodium, and aluminium are also able in the hot to extract two atoms of oxygen from CO_2, with separation of carbon; other metals, and carbon itself, reduce it at a red heat, removing one atom of oxygen, and forming carbon monoxide:

$$CO_2 + Zn = ZnO + CO \text{ and } CO_2 + C = 2CO.$$

In presence of heated carbon, CO_2 undergoes partial decomposition in accordance with the reversible equation: $CO_2 + C \rightleftarrows 2CO$; at 800° the percentages of CO_2 and CO by volume are 6·23 and 93·77 respectively, at 1000°, 0·59 and 99·41, and at 1200°, 0·06 and 99·94.

Chlorophyll, which is present in plants, reduces the atmospheric carbon dioxide under the influence of solar radiation and produces more or less complex carbohydrates which are utilised in the growth of the plant, oxygen being simultaneously liberated; vegetable cells also continuously absorb small quantities of oxygen with formation of CO_2.[1] At a temperature of over 1300°

---

[1] **Assimilatory and Respiratory Processes in Plants.** The most important substance absorbed by plants and transformed into the complex materials used to build up new tissues is carbon dioxide, which, by means of the chlorophyll of the chloroplasts and the action of sunlight is transformed into soluble carbohydrates (sugars such as glucose, etc.) with liberation of oxygen, this returning to the air to compensate for that withdrawn by living animal organisms of all kinds. All the carbon constituting plants is derived from the carbon dioxide assimilated from the atmosphere. In a tree reaching in thirteen years a weight of 500 kilos, about one-half consists of carbon (250 kilos correspond with 917 kilos of CO_2), and, since atmospheric air contains about 7 grams of CO_2 per 10 cu. metres, this one plant will have absorbed the CO_2 from 1,300,000 cu. metres of air, *i. e.*, 100,000 cu. metres or 70 kilos of CO_2 on the average per annum. The enormous number of plants on the earth might raise a fear that some day the air will be deprived entirely of CO_2. It has, however, been found that the content of CO_2 in the air has remained constant for about a century, owing to the existence in Nature of an infinite number of other organisms, more particularly animal, but also vegetable micro-organisms (yeasts, bacteria, etc.), which, in the exercise of their vital activity, fix oxygen from the air and from other food materials and emit carbon dioxide. Thus, every man expires daily about 900 grams of CO_2, so that for the whole 1,400 million inhabitants of the earth the production of CO_2 will be 1,200 million kilos per day. The 1,200 million tons of coal burnt per annum will give at least 3,600 million tons of CO_2, while large quantities are derived from the burning of wood, petroleum, spirit, illuminating gas, etc., and incalculable amounts are formed in all the fermentative and putrefactive processes of organic substances. From a very rough calculation, Heiden concludes that, at the earth's surface, there are produced annually about 86,000 million tons of CO_2, 82,000 million tons being fixed by vegetable organisms.

Not less important than assimilation in plants is the phenomenon of respiration. Particularly in green plants part of the substances assimilated is consumed in the process of respiration, which consists in a kind of oxidation or combustion of such part of the organic substances, with production of CO_2, H_2, and heat; in the latter originate all the vital processes. The heat produced by a pea plant is about 5 cals. per gram of its substance every twenty-four hours,

CO_2 is partly decomposed by repeated electric discharges into CO and O, but only a certain limited amount of the gas is decomposed, because the CO recombines with oxygen to form CO_2.

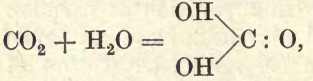
When carbon is burned in a given volume of oxygen CO_2 is formed without increase of volume, and this partly shows the composition of carbon dioxide: C (solid) + 1 vol. O_2 = 1 vol. CO_2.

The composition of CO_2 may also be shown by burning a given weight of pure carbon (diamond or graphite) in a current of oxygen and weighing the CO_2 which is formed, after absorbing it in a weighed solution of sodium hydroxide.

The heat of formation of CO_2 starting from carbon is: $C + O_2 = CO_2$: + 406 Kj. (97,000 cals.) per 12 grams of carbon or 44 grams of CO_2.

Dry CO_2 does not react with litmus paper, whilst when moist or in solution it shows a faint acid reaction, although when the paper is afterwards dried the red colour disappears. Solid carbon dioxide does not react with litmus paper.

In aqueous solution CO_2 probably forms the corresponding *carbonic acid:*



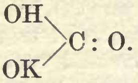
$CO_2 + H_2O = \begin{matrix} OH \\ OH \end{matrix}\!\!>\!C:O$, which, however, has not been obtained free, and appears to be stable only at 0° under a pressure of more than 12 atmospheres (Wroblewsky); when liberated from its numerous salts it immediately decomposes into H_2O and CO_2.

---

yet its temperature does not increase in comparison with the surrounding temperature, since the heat energy is partly dispersed and largely utilised in the elaboration and transformation of simple substances into more complex ones, until the albuminoids, etc., are reached. The oxygen for the oxidation is respired and absorbed from the air in the day-time and night-time by all the plant organs, whereas the green parts alone, and these only under the action of sunlight, assimilate CO_2 and emit oxygen. The plant, however, always increases in weight, this showing that the quantity of organic matter assimilated by the plant by means of its green parts alone and only in the day-time is greater than the amount of organic matter lost by the respiratory processes of all the organs. In one hour's assimilation the leaves accumulate as much material as would be consumed in thirty hours of respiration; however, the ratio between the volume of CO_2 absorbed and that of the oxygen emitted (*i. e.*, the respiratory quotient) is equal to unity.

Temperature and oxygen are the external agents which are capable of accelerating to some extent the respiration, although even pure oxygen cannot produce much acceleration (with pure oxygen compressed to 2 to 3 atmospheres the increase in velocity begins to become appreciable, and afterwards the plant tends to die). Without oxygen the plant is able to live and emit CO_2, the oxygen being withdrawn from the carbohydrate components of the plant (sugar, starch, etc.), but here also the plant tends to die as though poisoned, possibly by formation of carbon monoxide (intramolecular respiration), which is of great importance with seeds and in bacterial and fermentative processes, as described in considering the purification of waste waters (*see* p. 249; also chapter on Fermentation in Vol. II., "Organic Chemistry").

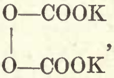
Of great interest are the experiments leading to the establishment of the influence of the quantity of CO_2 in the atmosphere on the growth of vegetation. As far back as 1873 Godlewsky stated that if plants live in an atmosphere containing, not the usual amount, namely, 0·033 per cent. of CO_2, but larger proportions, the functions of the plants are facilitated up to 8 to 10 per cent. of CO_2, whereas with a higher proportion the plants suffer. In 1888 Kreusler confirmed these results, but gave the limiting percentage of CO_2 as 13·5, and Pfeffer (1897) maintained that the phenomena of assimilation by the action of light and chlorophyll are also intensified. In some cases a double increase would be obtained, and it appears that the accumulation of carbon dioxide in the soil also plays a part. These facts furnish an explanation of the luxuriant vegetation in past geological epochs when the atmosphere was probably richer in CO_2 (*see* p. 335, Origin of the Atmosphere), and may also explain why the use of CO_2 in intensive cultivation has never been suggested, although for long the phosphorus, potash, and nitrogen removed from the soil every year by plants and crops are returned. H. Fischer and then R. Klein and E. Reinau (1914) have, indeed, questioned if the incomplete assimilation of fertilisers (about 60 per cent. of that applied to the soil) were not in part due to deficiency of CO_2 in the soil and air. In numerous culture experiments of different plants, Klein and Reinau found that the crop is 1·5 times and even twice as great with as without application of CO_2. That plants absorb CO_2 with avidity is shown by the fact that, with a still atmosphere, the air surrounding a dense vegetation (*e. g.*, beetroots) contains ten times less CO_2 than ordinary air.

It is a weak dibasic acid which forms secondary salts (disubstituted salts, carbonates) with strong bases; these show an alkaline reaction, owing to the feeble acidity of the acid. Monosubstituted salts, primary salts, *bicarbonates*, are also known, for instance:  $\begin{matrix}OH\\OK\end{matrix}\!\!>C:O$. The carbonates, other than those of the alkalis, are insoluble in water; the alkaline bicarbonates, on the other hand, are less soluble in water than the bicarbonates of the alkaline earths (Ca, Ba, etc.). The salts of carbonic acid are all decomposed by mineral acids and also by acetic acid with evolution of carbon dioxide.

CO_2 is in itself an almost harmless gas, but since it cannot maintain respiration, it may produce death by suffocation. This occurs when the expired air contains more than 15 per cent., because the liberation of carbon dioxide from the blue venous blood cannot then occur, and the lungs are no longer able to absorb oxygen. Even when the air contains 3 or 4 per cent. of CO_2 it produces a feeling of uneasiness which is followed by unconsciousness and all the symptoms of suffocation, and it is then necessary immediately to breathe pure air in order to regain the normal condition. In cellars or elsewhere where fermenting liquors are stored it is often dangerous to enter, and frequent accidents occur when ventilation is not provided there. This danger is detected by entering the cellar with a lighted candle, because it is extinguished by air containing more than 15 per cent. of CO_2.

For the quantitative determination of CO_2 in air, *see* p. 463.

CO_2 has also a mildly antiseptic action, and this partially preserves beverages such as wine and beer, and also meat, etc.

When a saturated solution of potassium carbonate is electrolysed at — 15°, the potassium salt of *percarbonic acid*, $H_2C_2O_6$, collects at the anode, being formed in an analogous manner to persulphuric acid. K_2CO_3 is first dissociated into $K^{\cdot}$ and $KCO_3{}'$ ions, and the latter are condensed at the positive pole, forming potassium percarbonate,  $\begin{matrix}O-COOK\\|\\O-COOK\end{matrix}$, which after drying forms a solid blue mass easily decomposed into $K_2CO_3 + CO_2 + O$; it is thus an energetic, oxidising agent, but may also act as a reducing agent, for the reasons explained on p. 266. Percarbonic acid is not known in the free state.

INDUSTRIAL PREPARATION OF LIQUID CO_2

Carbon dioxide has now found such large industrial application that it is necessary to explain the principal methods of manufacture, both in the state of pure gas and more especially in the form of liquid, for the production of cold, of ice, and for other purposes (*see below*). Liquid CO_2 was first applied industrially in 1878.

When gas from natural sources is very rich in CO_2 (more than 95 per cent.), it may be compressed directly and liquefied (after drying with calcium chloride or, better, sulphuric acid); if it contains other gases in sensible quantity it is concentrated by absorption by water under pressure (the absorptions of the separate gases are in proportion to their partial pressures, as explained in the succeeding footnote), diminution of the pressure then resulting in the liberation of a purer CO_2.

The sugar refineries, which do not require very pure CO_2, obtain it in the form of gas diluted with air (25 to 30 per cent. by vol. of CO_2), by heating limestone with coke in kilns similar to those used for the preparation of quicklime (*see* Part III), and in this way they also obtain lime for use in refining the sugar syrup. By heating dolomite (carbonate of Mg and Ca) or, better, magnesite, $MgCO_3$, in steel retorts, pure CO_2 is obtained; clay retorts are too porous. This process is still advantageous, if the residual magnesia can be utilised.

CO_2 may be obtained at relatively low temperatures (at a dark-red heat) from limestone, by heating it in a retort in presence of superheated steam.

In either case, however, it has been found in practice that at high temperatures the CO_2 rapidly attacks the retort.

Under certain special conditions, *i. e.*, when the resulting sulphate can be utilised, it is even to-day found convenient to prepare CO_2 by acting on a carbonate with sulphuric acid. Thus, in the case of the preparation of magnesium sulphate from $MgCO_3$ and H_2SO_4 (or $NaHSO_4$, a by-product of nitric acid works), CO_2 is obtained free of cost. In breweries to-day the carbon dioxide from the fermentation vats is also used after being purified by means of solutions of potassium permanganate, etc.

CO_2 is also prepared by the combustion of pure carbon, which must not contain tarry matter or hydrogen. For this purpose the coke from gas-works is especially suitable, though sometimes anthracite or wood charcoal is used, but the gas obtained contains only about 15 per cent. of CO_2; if Kindler furnaces are used (Fig. 190), a rather richer gas is obtained. The carbon is introduced through the opening, *b*, and is lighted at the base, *a*, *b* being then closed with a suitable cover. The amount of air necessary for combustion is drawn through the grate, *a*, by means of a pump which communicates with the apparatus through the tube *r*. The CO_2 formed passes while still hot, together with the nitrogen of the air, through the chamber, *c*, filled with limestone which retains the dust and the acid substances (SO_2), which develop further CO_2, this enriching the gas. The latter is cooled by passing over the bottom of the pans, *g* and *g′*, in which cold water circulates, is then washed in the vessel *d*, containing very dilute soda, to free it from dust and from sulphur dioxide derived from the sulphur always present in the carbon, and finally passes through the tube *r* to the gasometers. As the carbon in *b* becomes less in quantity, more material is introduced above. By this method, if the air current is carefully regulated, a gas is obtainable which contains a maximum of 20 per cent. of CO_2; in actual practice only 15 to 17 per cent. is obtained. For this reason the method is seldom used alone, but nearly always together with the preparation of bicarbonates from which all the CO_2 fixed is obtained again.

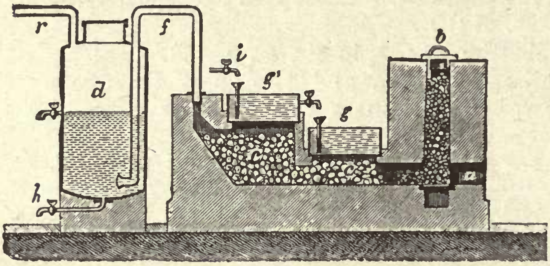


FIG. 190.

In order to prepare pure carbon dioxide, which may be used for liquefaction, the method of Ozouf is applied. He first prepares dilute CO_2 in Kindler's apparatus and then separates it from the other gases (O, N, and CO) by absorbing it in a solution of sodium or potassium carbonate at a temperature of 42° to 45° and a concentration of 20° Bé. Bicarbonates are thus formed which regenerate all the CO_2 at 100°. If the CO_2 has any smell it is first purified by passing through towers filled with animal charcoal which is cleaned occasionally by heating it to redness in a furnace.

Beins took out the first patent for obtaining liquid CO_2 directly from solid bicarbonate in 1878. He evolved the CO_2 by heating in closed vessels, so much pressure being thus exerted that the gas itself was liquefied (Faraday's method, *see* p. 28).

The industrial application of the method by forming bicarbonate solutions, together with a very ingenious arrangement of the apparatus for obtaining liquid CO_2, was first effected by Luhmann. From this time the liquid CO_2 industry extended rapidly, and numerous patents followed, marking an interesting series of improvements which it is impossible to describe, until the more recent processes have attained great practical success. In 1898 Raydt patented a process by the dry method, that is, by absorbing the CO_2 gas with dry carbonates in presence of the necessary quantity of steam to form the bicarbonates, and decomposing these with hot CO_2. This process, however, does not appear to have been successful in practice.

The new *Schütz process* has been applied in Italy (Candiani & Co. of Milan erected a works at Naples in 1908), and it differs from other processes in the fact that CO_2 and a certain quantity of pure distilled water are produced simultaneously. The latter is used both for steam boilers (thus avoiding incrustations) and also to dilute the solutions of soda (thus avoiding the accumulation of impurities by continued evaporation and dilution). The principle of lubricating the engine with the same solution of potassium carbonate is also employed, thus avoiding lubricating oils and the consequent contamination of the condensed water, which may also be employed for rediluting the solution of potash, etc. The heat which is developed through the combustion of the coke is sufficient to drive all the machinery; in fact the carbon is burnt in a semi-stationary engine of great efficiency and the combustion gases are utilised. The arrangement of the machinery and the stages of the process are shown diagrammatically in Fig. 191. The metallurgical coke (poor in S) burnt on the hearth heats the boiler, *a*, which supplies steam for driving the motor, *b*, lubricated with a solution of potassium carbonate. The gases from the coke are washed with a spray of water in the tower *c*, filled with coke, in order to free them from SO_2 and any ashes suspended in them. They escape from the top of this and are driven by the pump, *d*, through the saturating tower, *e*, from the top of which a spray of hot water falls. The hot gases are thus saturated with water vapour and enter the lower part of the absorption tower, *f*, from the top of which a spray of cold potassium carbonate solution falls. This not only absorbs the CO_2, but also condenses part of the moisture on account of the lowering of the temperature of the gases; thus there is no concentration of the potassium carbonate solution, which is, on the other hand, diluted. The gases which are not absorbed escape from the top of the tower *f*, and consist mainly of nitrogen which may be used as indicated above, whilst the solution, which is saturated with CO_2, is forced by the pump, *g*, through the gasifier, *h*, where by means of a bundle of tubes the hot solution (at 102°) of potassium carbonate, previously regenerated, is caused to circulate counter-current-wise; it then suffices to introduce a little exhaust steam from the engine (at 110° to 115°), in order to liberate the CO_2 from the bicarbonate together with part of the steam; the latter is condensed in the cooler, *i*, by means of a counter-current of water, the CO_2 being collected in the gasometer, *k*. The condensed water is used for the boiler, *a*, and the water which circulates in the cooler issues hot from the top and feeds the saturation tower, *e*, as has been described above. That part of the steam which is condensed after having heated the gasifier, *h*, is utilised by collecting the condensed water in *l*, in order to use it for feeding the boiler, *a*; it may also serve as pure distilled

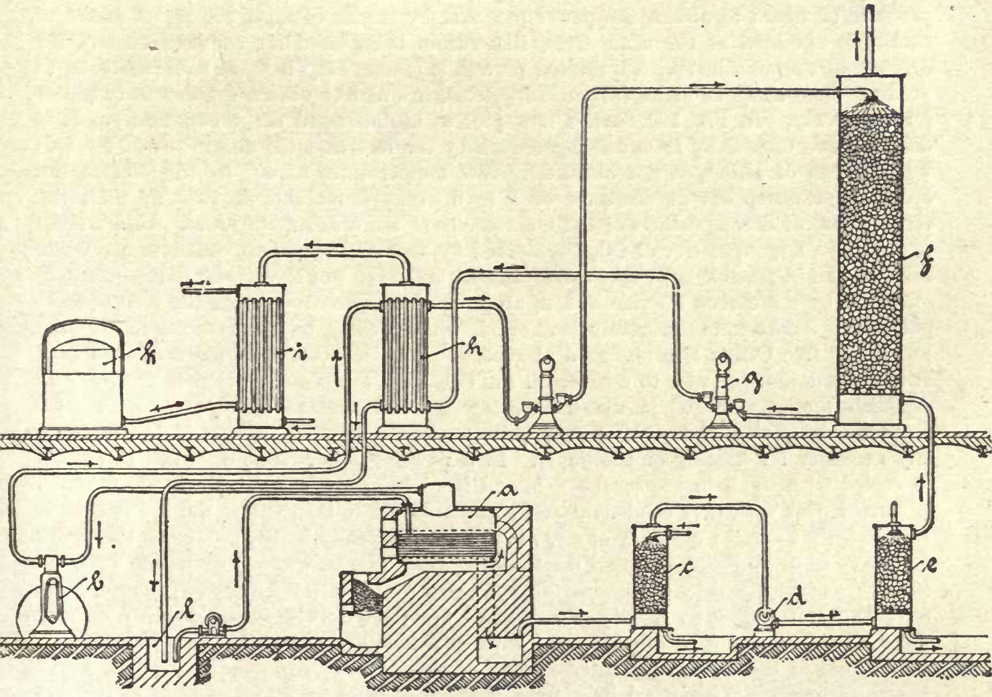


Fig. 191.

water, or for making crystalline ice (transparent) after de-aeration in a suitable apparatus with fractional condensation of the steam, or for diluting sulphuric acid for accumulators, or for washing photographic plates, etc. In any case there is abundant production of distilled water, which has a certain value if properly utilised. From the figure we see also how the potassium carbonate solution, freed from CO_2, is collected, and then pumped afresh into the absorption tower, *f*.

By this process also the heat produced by the combustion of the coke is rationally and almost totally utilised, and thus a yield of 1 kilo of pure liquid CO_2 of 99 per cent. is obtained from 450 to 500 grams of coke burnt.

For some years use has been made of the new Sürth process of the Sürther Maschinenfabrik at Sürth (near Cologne). This, instead of starting from dilute CO_2 (about 15 per cent.) from ordinary coke furnaces—by Kindler's process or others—starts from a more concentrated gas (almost free from oxygen) formed from suction gas (*see below*) in a gas engine, thus obtaining 1 kilo of liquid CO_2 from 0·5 kilo of coke. The coke is burnt in presence of steam to obtain the power gas, and by means of a gas engine an excess of energy is obtained at the same time, this excess being used for compression and for driving all the machinery. By the old process it is necessary to burn sufficient coke to produce three times as much CO_2 as is liquefied, in order to obtain the necessary power for the works. In Fig. 192 Sürth's new process is illustrated diagrammatically. It is distinguished essentially from other processes by the fact that the absorption of the CO_2 by solutions of K_2CO_3 is not effected at low temperatures of 40° to 45°, and at the ordinary pressure, but at pressures of 5 to 6 atmospheres and at 100° to 102°, the temperature of decomposition of the bicarbonate at the ordinary pressure. Under these conditions a large quantity of CO_2 is absorbed by half the volume of potassium carbonate solution and in much smaller apparatus, because on account of the greater partial pressure exercised by the carbon dioxide in a mixture of more concentrated gas the formation of potassium bicarbonate is greatly facilitated, while, owing to the compression of the gas itself,[1] free CO_2 is also absorbed at such pressures together with the combined CO_2. It is evident that in order to recover all the CO_2 from the bicarbonate it is necessary to diminish the pressure while the temperature of the solution is kept at 102°. The regenerated solution of K_2CO_3 is then quite ready for fresh absorption of CO_2 without any necessity for heating or cooling it. In *a* power gas is produced, which is washed or cooled with water in the scrubber, *b*, and freed from tar in *c*; in *d* the water which is carried over with it is condensed and separated, and it then enters the gas engine, *e*, with exactly the right quantity of air. It is here completely burnt, producing the power necessary to drive the works, and the resulting gases (exhaust gases) which are very hot (400°) are first utilised by circulating through tubes which keep the solution of bicarbonate contained in the gasifier, *f*, hot. These gases are then drawn by the pump *i* through the cylinders, *g* and *h*, which are filled with limestone and siliceous stones respectively. In the first of these they encounter a spray of water, while in *h* sulphur dioxide, which is always present, is absorbed by a weak solution of soda, and thus nothing is left but CO_2 and N. The same pump *i*, which is both a compressor and an exhaust pump, then compresses the gas to 6 atmos. and, after the lubricating oil carried in with it is separated, it is passed into the absorption tower, *m* (15 to 20 metres high and filled with coke, or arranged in chambers like the alcohol rectifying columns shown in Vol. II., "Organic Chemistry"), from the top of which falls the hot solution of potassium carbonate, which

---

[1] As regards the CO_2 which dissolves without combining in the potassium carbonate solutions, the partial pressure of CO_2 in a mixture containing 15 per cent. at the ordinary pressure would be $\frac{15}{100}$ of an atmosphere; in a gaseous mixture compressed to 5 atmospheres, on the other hand, the partial pressure of the CO_2 becomes $5 \times \frac{15}{100}$, that is, $\frac{75}{100}$ or $\frac{3}{4}$ of an atmosphere, and thus the absorption of the CO_2 is greatly increased compared with absorption at ordinary pressure. On the other hand, on working at ordinary pressure, as in the other processes, if of the 15 per cent. of CO_2 7 per cent. is absorbed by potassium carbonate solution in the first absorption tower, gas containing 8 per cent. of CO_2 will still be present in the second tower and the absorbed quantity will diminish rapidly, because the partial pressure of the CO_2 is decreased from $\frac{15}{100}$ to $\frac{8}{100}$ of an atmosphere; absorption in a third tower is rarely attempted. This explains how a considerable portion of the CO_2 produced in the coke furnaces is lost in the old processes, because it is not all absorbed by two or three potash towers. It may also be noted that only about half of the carbonate is transformed into potassium bicarbonate, and that above this limit the absorbing power of the potassium carbonate for CO_2 diminishes rapidly.

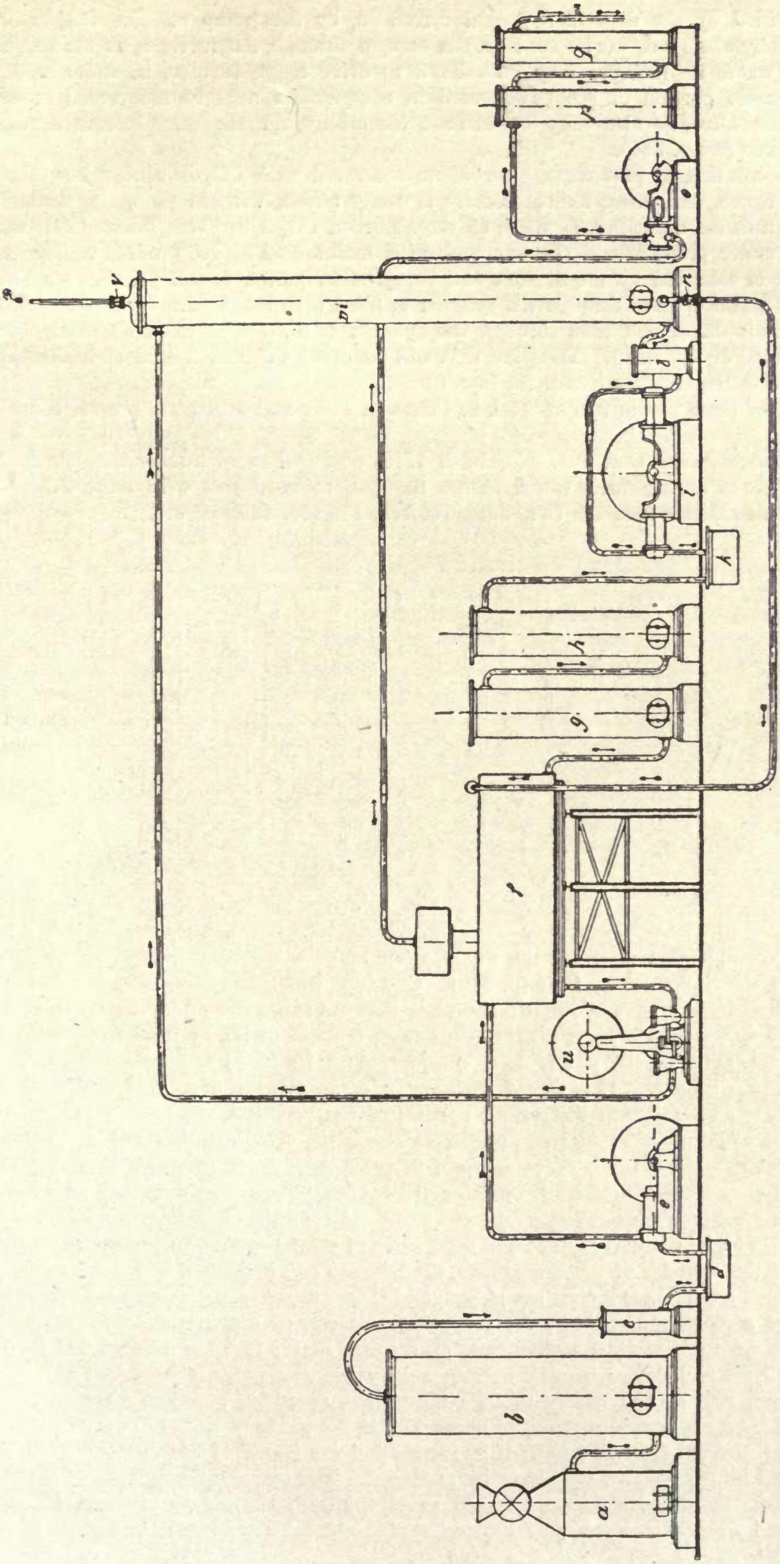


FIG. 192.

is provided by the degasifier, *f*, and forced in by the pump *u*. The CO_2 is almost completely absorbed, whilst the nitrogen escapes through the valve, *v*, at the top of the tower, where its pressure may be utilised to drive a gas turbine, in which manner a considerable portion of the power used in compression may be recovered; in certain cases the nitrogen also may be utilised chemically for the manufacture of calcium cyanamide (*see* p. 366).

The solution of potassium bicarbonate saturated with CO_2 is collected at the base of the tower, and being under pressure is easily raised, without pumping, through the tube *n* into the degasifier, *f*, where all the absorbed CO_2 is evolved, because it is here no longer under pressure and the temperature is maintained at 100° to 102°. The carbon dioxide is collected by the suction and compression pump, *o*, and passed at a pressure of 1 to 2 atmospheres through the cylinder *p*, filled with lumps of fused calcium chloride, where it is dried, and then through the cylinder *q*, filled with wood charcoal, where it is deprived of any smell. The pure, dry, and odourless CO_2 which is thus obtained finally passes into the true *compressor* for liquefaction.

One of these plants was at work in Genoa in 1906, and others are projected for other places.

F. Hildebrandt (Ger. Pat. 249,410 of 1910) obtained rapid liquefaction by means of an ingenious arrangement which allows the CO_2 to be cooled with solid CO_2. Other patents of interest here are Ger. Pats. 166,153, 173,130, 226,942, etc.

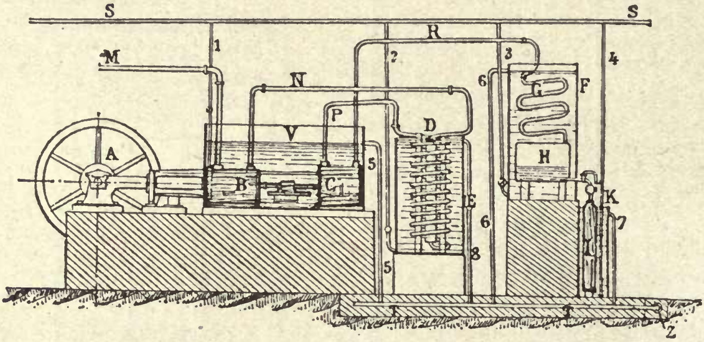


FIG. 193.

The compressors used for the liquefaction of pure CO_2 gas are analogous to those used for the liquefaction of air (p. 340). One type which has been used for some years, but has undergone several improvements, is that indicated diagrammatically in Fig. 193. The dry CO_2 gas, free from air, proceeds from the gasometer by means of the tube *M*, enters the body of the pump *B*, is compressed to 20 to 30 atmospheres, and escapes through the tube *N*. It is cooled with water in the serpentine coil, *D*, and then passes through the tube *P* into the second portion of the pump *C*, where it is compressed to 60 to 65 atmospheres. At this pressure it enters the cooling coil, *F*, where it is cooled with water, and accumulates as a liquid in the vessel, *H*, from which it is passed into the ordinary steel cylinders, *I*, used for transport. The compressors, the cooling coils, and the steel bombs are all surrounded by cold water, which circulates through the tubes 1 to 8. For lubrication glycerine is used and not oil, since this, in contact with the hot walls of the cylinder of the compressor, decomposes and imparts a bad smell to the CO_2. At various points manometers are placed, and there are safety valves on both compressors. In large modern compressors, the compression is carried out in three phases by means of three cylinders worked tandem-wise on a single shaft; it is compressed first to 4 to 5 atmospheres and cooled in coils surrounded by running water, then to 30 atmospheres and again cooled, and finally to 65 atmospheres, at which pressure, after cooling, the liquid CO_2 is charged into the steel bombs. For the production of 10 kilos of liquid CO_2 per hour, the coil *D* has a length of 80 metres and *F* a length of 150 metres. With 6 h.p. 20 to 25 kilos of liquid CO_2 may be produced. The cylinders containing the CO_2 are similar to those used for compressed gases (pp. 138, 192); they are cast in a single piece, and when of a capacity of 10 litres should not contain more than 8 litres of liquid

CO_2 (= 4360 litres of gas) in order to avoid accidents through the very great dilatation of the liquid CO_2 (*see* p. 471).[1]

Modern cylinders are provided with safety valves which open automatically at temperatures of 80° to 100° (suitable fusible metal plugs being used), so that in case of fire the valve may fuse and liberate the gas, danger of explosion being thus avoided.

We shall now illustrate by a practical example the thermal balance of the industrial process, just as has already been done for the manufacture of hydrochloric acid (p. 177).[2]

Liquid CO_2 is placed on the market, as we have already said, in steel cylinders of various sizes (*see above*).[3] These are closed above by means of various pieces strongly screwed together, as is seen in Figs. 194 and 195, which require no further explanation,

---

[1] The cylinders weigh 37 kilos; after being made they must be heated to redness before being subjected to the Italian official test of resistance to a pressure of 190 atmospheres (re-tested every three years), although ordinarily they have only to sustain a pressure of 60 to 70 atmospheres. They are so safe that the railways (in Italy) to-day allow them to be carried on all trains, whereas at first they were classed with inflammable and explosive materials. It has now been shown that, with a normal filling of 1 kilo of liquid CO_2 per 1·34 litres of space, the cylinder is completely filled with the liquid when the temperature exceeds 22° (given its high degree of expansion), but that there is even then no danger, since the liquid has such a high coefficient of compressibility (0·002259 at 15°). In order that the pressure of 190 atmospheres (at which the cylinders are tested) may be exceeded, it would be necessary for the external temperature to exceed 52°, at which temperature (beyond the critical temperature, 31°) the contents of the cylinder are all gaseous.

[2] For a factory which produces 50 kilos of liquid CO_2 per hour by the coke furnace process, about 15,000 litres of potassium carbonate solution of 20° Bé. are required, weighing 17,430 kilos, the whole of which has to be heated from 45° to 102° (by the old process) in order to generate the CO_2 which is absorbed. In order to raise the temperature in this manner by 57° about 993,500 Cals. will be required (that is, 17,430 × 57 Cals.) (*a*), to which we must add about 53,600 Cals. (*a′*), because about 100 kilos of water are evaporated together with the CO_2, and the heat of evaporation of water is 536 cals.

Furthermore, for working the compressors, pumps, transmitters, etc., a steam engine is required of about 25 h.p. which consumes per hour 375 kilos of steam at 5 atmospheres pressure, that is, 15 kilos per h.p.-hour. For this production of steam, 62·5 kilos of coke are required, as, generally speaking, 1 kilo of coke produces 6 kilos of steam, that is, 1·25 kilos of coke (*b*) are required for each kilo of liquid CO_2 manufactured $\left(\frac{62{\cdot}5}{50} = 1{\cdot}25\right)$.

A portion of the heat produced during all these processes is recovered in the following manner: The 62·5 kilos of coke produce on burning 312,000 Cals. (*c*) (5000 for each kilo), and of this only 251,000 Cals. (*d*) are utilised for the production of 375 kilos of steam at 5 atmospheres pressure, that is, at a temperature of 153°; for, in order to raise 1 kilo of water from 20° to 153°, 133 Cals. are required, and to convert this into steam at 5 atmospheres a further 536 Cals. are needed, being 669 Cals. altogether, and thus for the 375 kilos of steam we require 375 × 669 = 251,000 Cals.; the remaining 61,000 Cals. (*e*) remain in the hot furnace gases from the coke furnace, and of these about 50,000 Cals. (*f*) are recovered by heating the solution of potassium bicarbonate. On the other hand, the degasified solution of carbonate at a temperature of 102° must be cooled to 45°, and during this process serves in a counter-flow apparatus to heat the bicarbonate solution to be gasified. It is calculated that about 44° of this temperature difference can be utilised, and for 17,430 kilos of solution this gives a recovery of heat of 766,900 Cals. (*g*). Finally, we may calculate the recovery of the heat which escapes from the steam engine, supposing that 10 per cent. of this is lost by prior condensation, leaving 338 kilos of steam at 100°; this 338 kilos of steam may be condensed in heating coils in the degasifier, and thus regenerates 338 × 536 = 181,170 cals. (*h*). We thus obtain the following summary :

	Heat employed		Heat recovered
(*a*)	993,500 Cals.	(*f*) . . .	50,000 Cals.
(*a′*)	53·600 ,,	(*g*) . . .	766,900 ,,
(*c*)	312,000 ,,	(*h*) . . .	181,170 ,,
Total . .	1,359,100 Cals.	Total .	998,070 Cals.

The difference is, therefore, 361,030 Cals., which are necessary for the production of 50 kilos of CO_2; since 1 kilo of coke yields 5000 Cals. 72·2 kilos of coke will be necessary for this purpose, that is to say, in order to produce 1 kilo of liquid CO_2, we require by this process 1·44 kilos of coke altogether, and this result is confirmed by actual experience.

[3] In the United States it is required that the steel used for such cylinders shall contain less than 0·55 per cent. C, 0·04 per cent. P, and 0·05 per cent. S, that the elastic limit shall be 5000 to 6000 lbs. per sq. inch, and that the elongation of a strip 8 inches long cut longitudinally should be at least 10 per cent.; with an internal water pressure of 3000 lbs. per sq. inch the permanent expansion should not exceed 5 per cent. of the total expansion; the walls of the cylinder should be at least ¼ inch thick, and the normal cylinder of the dimensions 8½ × 51 inches should weigh 105 to 115 lbs.

because one can see how by turning the upper valve the escape of CO_2 may be readily regulated, and how a side-piece may be attached containing a pressure-reducing valve. For each kilo of CO_2 2 kilos by weight of steel cylinder are needed, from which it is evident that it is not profitable to transport CO_2 to great distances, because whilst the product itself costs 1*d.* to 1½*d.* per kilo, the freight and return of the empty cylinders to distances of 300 to 400 km. (200–250 miles) cost 1*d.* to 1¼*d.* (in Italy) by goods train and 3*d.* to 3½*d.* by passenger train. The cylinders for 10 kilos of liquid CO_2 weighed at one time 42 kilos (in welded iron), but those now made in England and Germany (also in Italy and France) from steel drawn in a single piece weigh 23 kilos; formerly they cost 64*s.* each, but more recently the price has fallen to less than 16*s.*

The factory of Rommenhöller in Berlin alone possessed before the war 155,000 steel cylinders for the transport of liquid CO_2.

SOLID CARBON DIOXIDE. This is formed with relative ease as a white mass similar to snow by allowing liquid carbon dioxide to expand rapidly and freely in the air. Natterer allowed liquid CO_2 to expand in a brass chamber, whilst Landolt in 1884 obtained solid CO_2 in a much simpler manner by placing a woollen bag over the mouth of a cylinder of liquid CO_2 which was inclined downwards; on opening the valve the CO_2 solidified as a snow in expanding and was retained by the bag, whilst the gas passed out through its pores. On compressing this solid CO_2 in cylinders it is obtained as blocks of solid CO_2 which are very compact and have a specific gravity of 1·2; they evaporate very slowly, and by simply wrapping them in cardboard, cotton wool, or other substances, they may even be despatched without any danger by rail, just in the same manner as ordinary ice. By spontaneous evaporation their temperature remains at — 65° (*see* p. 472). Attempts have been made in England to establish a trade in this product (Eng. Pat. 21,861 of 1899), and it is probable that it may acquire importance in the future, as it would be easy to produce great cold very cheaply without danger and without machinery, by the use of solid CO_2, the cost of transport being greatly reduced owing to the heavy and costly steel cylinders being dispensed with. Recently, in 1905, a company for the preparation and sale of solid carbon dioxide was established at Charlottenburg, using the process of Heyl and Wultze (Ger. Pat. 157,403); the compressed product is placed in receivers in which only the atmospheric pressure is maintained; these are surrounded by a freezing mixture and communicate with a small compressor.

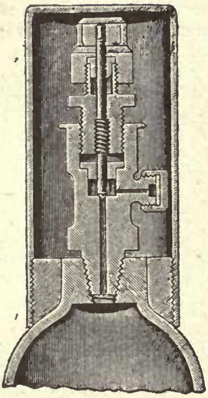


FIG. 194.

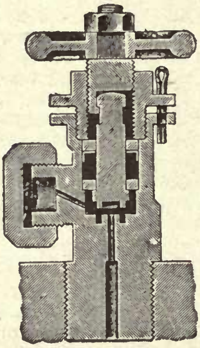


FIG. 195.

Solid carbon dioxide is soluble in acetone, alcohol, ether, and light petroleum. When 50 grams of solid CO_2 are dissolved in 150 grams of acetone, a solution is obtained which shows a temperature of — 63°, and is used for many laboratory purposes.

APPLICATIONS OF CARBON DIOXIDE. The gas is used in sugar refineries for separating from the sugar juice the lime which has been used for defecation. It is also used in white lead factories and in the manufacture of bicarbonates and of Solvay soda.

Liquid carbon dioxide is also used for effervescing drinks, such as soda water, mineral waters, sparkling wines, etc., because it holds certain salts in solution which would otherwise be precipitated (*see* p. 256); in beer and wine it has also a preservative action and hinders decomposition.

In restaurants the beer is raised from the cellar by connecting the barrel with a cylinder of liquid CO_2 furnished with a reducing valve, *B* (Fig. 196), and thus forcing it through the concentric tube, *G*, to the delivery tap. It is thus kept saturated with CO_2.

Raydt suggested the use of liquid CO_2 contained in iron cylinders at great pressure (about 60 atmospheres) for motors and also for projecting water to great distances in case of fire without the use of a pump. Liquid CO_2 is largely used in breweries for the preservation and saturation of the beer and in the pressure apparatus which serves to convey it. It is used in ice factories (p. 264), and its use has been proposed for removing boiler scale by saturating the feed water. It is now used in large quantities for hardening white metal and steel and for obtaining large steel castings without blowholes; for this purpose liquid CO_2 is poured on to the steel castings in gas-tight vessels, enormous pressures being thus produced at high temperatures (about 700 atmospheres at 100° and about 2000 atmospheres at 200°). Under these conditions the solidified casting is free from blowholes. The firm of Krupp of Essen use about 100 kilos of liquid CO_2 per hour for this purpose, especially for the casting of guns of large calibre. It is also used as an anæsthetic and generally for producing cold for surgical operations.

It is further employed to freeze sandy or crumbly soil before this is bored or excavated for wells, canals, foundations for the pillars of bridges under the water level, etc. At points where boring is to be carried out, a series of communicating vertical tubes are driven into the ground forming a ring of a diameter about two metres wider than the proposed boring. In these tubes brine from an ice machine is circulated or liquid carbon dioxide is evaporated. The previously moistened soil freezes and the whole forms a rigid block which may be easily and safely excavated. The great pressure of CO_2 in steel cylinders is also used for raising sunken ships, to which a deflated balloon is attached, which is then filled with compressed gas—CO_2, hydrogen, etc.—under water, the balloon thus raised carrying the submerged vessel to the surface. Compressed CO_2 is also used for decanting inflammable liquids (benzene, etc.).

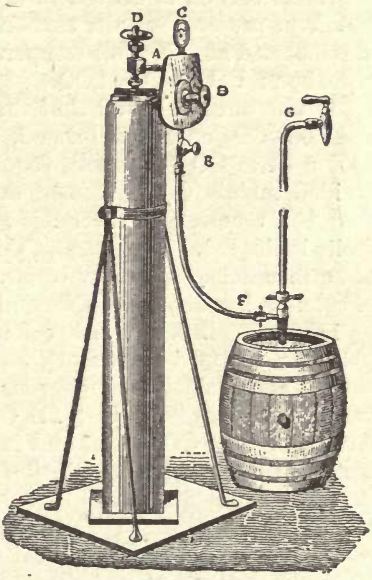


FIG. 196.

PRICES AND STATISTICS. In Germany in 1884 122 tons of liquid CO_2 were produced, and in 1889, 1000 tons; in 1891 there were 23 works manufacturing liquid carbon dioxide which produced 2000 tons and exported about 1000 tons. In 1899 there were 60 works producing 14,000 tons of liquid CO_2, more especially provided by natural springs and the combustion of coke, and a smaller quantity by heating carbonates. Practically none is to-day prepared from carbonates with mineral acids. In 1905 the production rose to 30,000 tons (two-thirds obtained from natural gas), of which 7332 tons were exported at a price of 1*d.* per kilo in steel cylinders supplied by the purchaser; it costs ½*d.* a kilo more when the cylinders are supplied by the manufacturer. In 1909 the production increased to 15,000 tons and the exports diminished to 2641 tons; in 1910 the output was 34,000 tons.

In France there are fewer works. The Carbonique Lyonnaise produces 150 kilos of liquid CO_2 per hour, and always maintains a stock of 13,000 cylinders of CO_2. The works at Bobigny produce 100 kilos per hour by burning coke. In 1897 France produced barely 1000 tons of liquid CO_2, while in 1900 it produced 8000 tons and the price descended from 1*s.* 3*d.* per kilo to less than 4*d.* per kilo, through competition. In Germany small quantities of liquid CO_2 are also sold at 2½*d.* to 4*d.* per kilo. In 1906 there were 40 works in the United States of America with a production of 15,000 tons. Switzerland produced 350 tons in 1905.

In order to *analyse* liquid CO_2 a sample is taken in a weighed glass tube with two cocks, by connecting it with the inverted steel cylinder so that liquid CO_2 is removed and not the gas mixed with air which is above it. From the weighed glass tube a portion of the gas is then passed into an Orsat apparatus in order to be analysed in the ordinary way (*see* p. 463).

As a general rule liquid CO_2 contains only 0·1 to 0·2 per cent. of moisture and up to 2 to 3 per cent. of air; sometimes it contains also as much as 3 to 4 per cent. CO. At the bottom of the cylinder there is often a little water and glycerine (the latter used as lubricant in the compressors), which should not exceed 50 to 70 grms. per 10 kilos of liquid CO_2.

CARBON MONOXIDE: CO

When carbon is heated to a temperature of 700°, or better still to above 1000°, in presence of air, carbon monoxide is mainly obtained instead of the dioxide, and at this same temperature CO_2 is decomposed in presence of excess of carbon: $CO_2 + C = 2CO$.

It was once believed that during the combustion of carbon between 400° and 700° CO_2 only was formed, but it has recently been shown that even at 500° a little CO is formed, together with the CO_2, and in presence of finely divided metals CO is formed even at 300°. This is explained by the fact that the reaction is reversible: $C + CO_2 \rightleftarrows 2CO$, between the temperature limits indicated. In general, CO is formed whenever carbon is burnt in presence of an insufficient quantity of air. Also in the wet, with an oxidising solution of calcium hypochlorite, CO_2 and up to 9 per cent. of CO are produced.

PROPERTIES. It is a colourless, odourless gas, almost insoluble in water (3·3 vols. in 100 vols. water), but is very soluble in an ammoniacal or hydrochloric acid solution of cuprous chloride, with which it forms a crystalline compound, $Cu_2Cl_2, 2CO + 2H_2O$; when heated with potassium hydroxide the latter liberates CO again, and is separated as a black precipitate. A concentrated calcium chloride solution absorbs fifteen times its own volume of CO.

Even small quantities of CO produce a black precipitate with a solution of palladium chloride; as little as 0·5 per cent. of CO in air gives a brown coloration with an ammoniacal solution of silver nitrate, which then gives a black precipitate when boiled.

With iodine pentoxide, I_2O_5, it gives a fairly sensitive reaction by liberating iodine, which forms a violet solution with chloroform or carbon disulphide:

$$5CO + I_2O_5 = I_2 + 5CO_2.$$

It is decomposed quantitatively by calcium carbide at 250°, with formation of calcium oxide and graphitic carbon: $CaC_2 + CO = CaO + 3C$. This reaction was utilised by Frank and Caro (*see* p. 143) to eliminate CO from water gas and so prepare industrial hydrogen. According to Ger. Pat. 254,043 of 1911, even traces of CO may be removed from its mixtures with other gases (*e. g.*, nitrogen and hydrogen as used for synthetic ammonia, *see* p. 373) by fixing it with concentrated caustic soda solution (80 per cent.) at a pressure of 50 atmos.

It is lighter than air (0·9672), and 1 litre weighs 1·2508 grms. Its critical temperature is − 141°, and its critical pressure 35 atmos. Liquid CO boils at − 190°, and becomes solid at − 212°. Its specific heat is 0·2370 at constant pressure and 0·1684 at constant volume.

In the gaseous state it burns with a fine bluish flame, and when 2 vols. of CO are mixed with 1 vol. of oxygen in a cylinder and lighted with a powerful flame, a detonation is obtained: $2CO + O_2 = 2CO_2$. If the gaseous mixture is moist it is ignited very easily and at a lower temperature, perhaps because the CO first reacts with water vapour forming hydrogen: $CO + H_2O = CO_2$

$+ H_2$, and the hydrogen in turn combines with the oxygen of the mixture, regenerating water, so that in this case the latter would exert a pseudo-catalytic action. The flame of CO is extinguished in perfectly dry air, and a perfectly dry mixture of CO and air does not explode, although it does so if a trace of moisture is present.

Being a gas which is still oxidisable it has the property of reducing various metallic oxides, for example, copper oxide, at a red heat:

$$CO + CuO = CO_2 + Cu.$$

It also reduces certain oxides and chlorides of the noble metals even in the cold. A sensitive reaction for CO is thus obtained with a piece of paper impregnated with palladium chloride, which blackens in presence of traces of the gas.

CO does not maintain combustion because it yields up its oxygen with difficulty, only separating carbon by the action of potassium at a red heat. A mixture of CO and H under the action of the dark electric discharge yields formaldehyde, which is one of the simplest organic compounds known: $CO + H_2 = HCOH$.

It is a very poisonous gas even in small quantities, as 1 litre of CO in 100 cu. metres of air produces symptoms of poisoning, and 1 litre in 779 litres of air is capable of killing a man in half an hour. When absorbed by the blood it may be recognised by means of the spectroscope.[1] It combines with the hæmoglobin of the blood, thus preventing the formation of oxyhæmoglobin and the vital functions of the blood, through anoxæmia.[2] The symptoms of carbon monoxide poisoning are headache, unconsciousness, convulsions, etc. Air which contains only 0·05 per cent. is poisonous for human beings, and cases of poisoning in badly ventilated rooms in which coal is burnt and where the stove is made of iron which becomes porous when hot are thus explained. In such cases the fuel is burnt with an insufficient quantity of air and at very high temperatures. In speaking of oxygen (p. 190) we directed attention to the experiments of Mosso, who showed that in compressed oxygen animals resist the action of 6 per cent. of CO, but that when the pressure is released the animals immediately die.

PREPARATION. When an electric arc is passed between carbon electrodes under water CO is formed at the expense of the carbon of the electrodes: $C + H_2O = CO + H_2$.

Various organic acids, such as citric, malic, oxalic, and formic acids, when treated on the water-bath with strong sulphuric acid (monohydrate), develop a strong current of carbon monoxide mixed with very little carbon dioxide. In the laboratory oxalic acid is always used and the traces of CO_2 are separated by passing the gas through a solution

---

[1] The blood, diluted with water to a pale pink colour, is placed in a glass vessel with parallel faces 1 cm. apart; light passed through it is collected in a spectroscope, two absorption bands between the lines *D* and *E* being observed. On addition to the blood of a few drops of concentrated ammonium sulphide solution, these bands remain distinct if CO is present, but otherwise are transformed into a single black band. As little as 0·03 per cent. of CO in air is detectable by placing a rat under a bell-jar with 10 litres of the air, drowning the rat at the expiry of two hours and examining a couple of drops of blood (diluted with water) from its heart in the spectroscope. Another method consists in passing the air through a neutral palladium chloride solution, palladium being then precipitated in proportion to the amount of CO; the metal is dissolved in *aqua regia* and the solution titrated with potassium iodide.

[2] P. Giacosa maintains, on the other hand, that death occurs from a different cause, namely, through a reflex paralysis of the nervous centres governing respiration, caused by contact of the carbon monoxide with the sensitive terminals of the respiratory passage. Thus it is a case of poisoning, not by chemical, but by nervous action.

Many theoretical considerations and certain experiments of Marcacci also point in this direction. The experiment conceived and carried out by Giacosa is of interest in this connection. He first removed the blood from a dog and then, when it was at the point of death through acute anæmia, he introduced into its circulatory system the blood of another dog which had already been treated with carbon monoxide, so that its red blood-corpuscles no longer contained any oxygen. The entry of this blood into the respiratory system of the dog caused the respiratory activity to be revivified at once, and the dog immediately regained normal respiration and passed in a few minutes from death to life. Thus, as in this case the blood which circulated in the body of the revived dog contained, at least at the beginning, quantities of oxygen much less than those which remained in the blood of an individual killed by poisoning with carbon monoxide, we may conclude that in such individuals death occurs through other causes.

of sodium hydroxide. (*Translator's note.*—In these cases the amounts of carbon dioxide formed may be considerable and from oxalic acid equal volumes of CO and CO_2 are formed.)

The preparation from potassium ferrocyanide (1 part) with strong sulphuric acid (9 parts) is even more convenient. In this case the gases are passed through a solution of sodium hydroxide to absorb the traces of CO_2, SO_2, and prussic acid which are always formed.

A purer gas may be obtained in larger quantities by adding formic acid (sp. gr. 1·2) drop by drop to concentrated sulphuric acid heated to 140° to 160°, the gas being dried over potassium hydroxide: $H_2CO_2 = H_2O + CO$.

CO may be obtained from CO_2 by powdered metallic zinc heated to dull redness: $CO_2 + Zn = ZnO + CO$, or more easily by heating magnesium carbonate mixed with zinc dust in a retort; a mixture of $CO_2 + CO$ is first formed, but pure CO is obtained later; the magnesium carbonate may be advantageously replaced by calcium carbonate:

$$CaCO_3 + Zn = ZnO + CaO + CO.$$

On heating carbon with metallic oxides CO is also formed, thus $C + ZnO = CO + Zn$, and this reaction explains the reducing action of carbon on heating with various metallic oxides, which is utilised in the preparation of metals.

Carbon monoxide is of direct use only in exceptional cases, but it appears to have been largely employed during the European War for filling asphyxiating and poisonous gas shells, being obtained in abundance in the manufacture of hydrogen from water gas (*see* p. 143). The latter, containing carbon monoxide and hydrogen, together with a little CO_2, N, etc., is used as a source of heat, light, and motive power.

WATER GAS. As an illuminant water gas was useless until the discovery of the Auer mantle, as there was always danger of poisoning in cases of escape or incomplete combustion owing to the high content of CO; for this reason many attempts were made to diminish the percentage of CO as far as possible.[1]

---

[1] In 1832 Gobard, of Brussels, used this gas for illuminating purposes, but with unsatisfactory results.

In spite of the improvements of Selligne and then of Witte, Leprence, Baldamus, Grüne, Isoard, Kirkham, etc., by which the gas was rendered luminous by mixing it with hydrocarbons such as benzine, it was not used in large quantities. In 1860 Fayes constructed an apparatus by which a water gas containing little CO was prepared by employing an excess of steam in order to transform the CO partly into CO_2: $CO + H_2O = CO_2 + H_2$ (for percentage composition *see below*).

On cooling, this gas deposits the excess of steam, and then, when passed over calcium hydroxide the CO_2 is absorbed, leaving almost pure hydrogen. By means of his apparatus Fayes produced as much as 1200 cu. metres of hydrogen per twenty-four hours at a cost of about ½*d.* per cu. metre, exclusive of labour and the cost of plant. This method was fairly successful at first, but was abandoned on account of the not inconsiderable technical difficulties. The method was only taken up again about the year 1880, first by C. Hessel in Kilburn (Eng. Pat. 3584 of 1880), then by G. E. Moore of New York in 1886 (Ger. Pat. 35,203 of 1886), and finally by Hembert and Henry in 1886 with a very ingenious arrangement of plant.

In the latter apparatus the superheated steam in small jets is first brought into contact with red-hot coke in the first retort; equal volumes of CO and H_2 are thus formed and are passed into a second red-hot retort filled with lumps of refractory fireproof stone, and the reaction is completed by means of jets of superheated steam: $H_2O + CO = H_2 + CO_2$. The gas finally contains H_2 and CO_2 only, and when it is passed over lime, hydrogen alone remains. Boulogne-sur-Seine is lighted on this system. The gas is rendered luminous by placing a small platinum net in the middle of the flame, as had been proposed by Giffard in 1846. This gas costs about 1½*d.* per cu. metre.

According to Eng. Pat. 2523 of 1909 carbon monoxide may be economically removed from water gas and replaced by hydrogen by passing the gas mixed with steam at 500° into a hot cylinder containing calcium hydroxide, $CaCO_3$ and H_2 being thus obtained; the CO_2 remains fixed by the lime.

The excess of water vapour proposed by Fayes and applied by Hembert and Henry in order to obtain less CO is advantageous on account of the mass law, because, given the following systems in equilibrium, of the following possible reactions:

$$(1)\quad C + H_2O = CO + H_2 \qquad (3)\quad CO_2 + C_2 = CO + CO$$
$$(2)\quad C + 2H_2O = CO_2 + 2H_2 \qquad (4)\quad CO + H_2O = CO_2 + H_2,$$

the simplest and most economical means of displacing the equilibrium in such a manner as to produce less CO (1 and 3) and more hydrogen, is by increasing the velocity of the reactions (2) and (4), that is, by increasing the quantities of steam or by removing the CO_2, as was actually done later. It is true that the reaction (1) occurs at high temperatures with absorption of heat corresponding with 133 Kj. (= 31,800 cals.), and that reaction (2) occurs at lower temperatures, but also with absorption of heat, namely, of 91 Kj. (= 21,750 cals.) In order to start the reaction

The most important uses of water gases are for the production of heat and motive power.

The water gas industry has developed considerably, first in the United States, where there is abundance of anthracite which contains very little bituminous matter and hence lends itself well to the production of water gas. In Europe its development has taken place more especially since 1890 as a result of investigations made by Bunte, Quaglio, Schiele, Blass, etc., which led to the use of coke in the manufacture.

As early as 1794 Courbelle found that steam in presence of carbon heated to about 600° forms CO_2 and H, thus: $C + 2H_2O = CO_2 + 2H_2$, but that above 900° CO is mainly formed: $C + H_2O = CO + H_2$, and $CO_2 + C = 2CO$. It is necessary to remember that during this reaction, and in the production of water gas, absorption of heat occurs,[1] so that the working of producers for making water gas requires regulation. The reaction being endothermic, the passage of the steam over the glowing coal almost extinguishes the latter unless the steam is alternated every 5 to 6 minutes with air, which produces CO_2 and a considerable rise in temperature.

The old form of water gas producer worked somewhat as follows: a current of air is passed for about 7 to 12 minutes into the layer of glowing coke, which is 2·5 to 3 metres deep, the air gas (*see below*) formed during this period being partly used to heat the boilers in which the steam necessary for the succeeding phase is generated, the remainder being wasted if it cannot be utilised. When the coke is quite red hot, the entry of air at the top is stopped and steam passed in at the bottom, this being converted into water gas, which issues from the lower part of the producer to be washed and cooled in a scrubber and then collected in a gasometer. In order that the glowing coke might not be extinguished, this second phase formerly lasted only 5 to 6 minutes, and was followed immediately

---

it is, therefore, necessary at the beginning to supply heat by means of superheated steam or to introduce a little air, which unites with the carbon to form CO and thus develops heat.

The disadvantage of this process is the presence of a larger or smaller quantity of CO; excess of steam is eliminated by drying the gas with H_2SO_4—1 kilo per 100 cu. metres of gas.

The elimination of CO was also attempted by Bauer (1887) by adding iron oxide to the fuel. This was reduced to metallic iron partly by the carbon and partly by the CO.

Pritschi and Beaufils in 1887 proposed the absorption of the CO by means of a solution of cuprous chloride, Cu_2Cl_2, which was then recovered by liberating the absorbed CO *in vacuo*.

A *water gas* obtained by the interaction of steam and carbon and purified with CaO only (to absorb the CO_2) gave the following results on analysis: H = 36 per cent.; CO = 51 per cent.; N = 7 per cent.; CO_2 = 4 per cent. A gas of this kind, on account of the high temperatures produced during combustion and the enormous quantities of CO, cannot be used for illuminating purposes. In certain cases the CO forms 40 per cent. and hydrogen 50 per cent. of the mixture.

In 1893 the firm of Krupp of Essen (Ger. Pat. 67,827 of 1893) improved the process by the use of the method of Tessié du Motay and Maréchal (1868). They mixed calcium oxide with the fuel so that the CO_2 was at once fixed as fast as it was formed, and the production of CO thus prevented.

Krupp obtained considerable advantages by mixing the fuel with carbonates and hydroxides of the alkalis or alkaline earths; in this way a gas composed of H_2 and CO_2 only was at once obtained as soon as the action of the steam commenced at a fairly low temperature. In this reaction air is excluded and thus no nitrogen is present in the resulting gases.

This water gas is not poisonous and may be employed directly as a fuel gas and for heating. From this gas pure hydrogen and pure CO_2 may be obtained if desired by liquefying the CO_2 by pressure and refrigeration.

In North America water gas has been advantageously employed instead of ordinary lighting gas, by carburetting it with light petroleum in order to render it luminous, as had been shown by Lowe, helped by the discoveries of Faraday, who had shown that the flame of methane gas may be rendered luminous by passing it over liquid hydrocarbons. Water gas may be employed very economically to-day by rendering it luminous by means of the Auer mantle, formed of oxides of zirconium, thorium, etc. (*see later*), which easily become incandescent, emitting a very white light.

[1] The dissociation of 1 gram-mol. of water vapour requires 57,600 cals., whereas the formation of 1 gram-mol. of CO is accompanied by liberation of 29,300 cals., so that: $C + H_2O = CO + H_2 - 28,300$ (*i. e.*, 29,300—57,600). Also, since the formation of 1 gram-mol. of CO_2 leads to the development of 97,700 cals., the reaction $C + 2H_2O = CO_2 + 2H_2 - 17,500$ cals.

An ideal water gas, formed according to the equation, $C + H_2O = CO + H_2$, should yield equal volumes of CO and H_2, and its calorific value per 1000 litres of the gas may be calculated as follows: 500 litres of hydrogen weigh 45 grms., and since the combustion of 2 grms. of hydrogen to water yields 57,600 cals., 45 grms. will give 1296 Cals. (= 1,296,000 cals.); then 500 litres of CO weigh 623 grms., which (since 1 grm. of CO gives 2420 cals. when burnt to CO_2) will yield 1520 Cals. Hence, altogether, 1 cu. metre of the ideal water gas has a calorific value of 1296 + 1520 = 2816 Cals.

by the air gas phase, etc., so that of every hour 40 minutes were used in producing air gas (partly unusable) and only 20 in the production of the required water gas. In the Dellwik and Fleischer producer (Ger. Pat. 105,511, Dec. 1896) the coke is heated more rapidly by passing in sufficient air to form CO_2 directly, 8080 cals. being thus developed in place of 2400 cals. for CO; the formation of air gas then occupies only 1 to 2 minutes for every 7 minutes taken to make water gas, the production of the latter thus occupying about 50 minutes per hour. Fig. 197 shows diagrammatically a Dellwik and Fleischer plant. The producer *G* is charged with coke or anthracite and is at first lighted with wood, the double valve, 3, and the discharge orifice, 5, being opened and the valves 9 and 9′ closed. By means of the fan, *V*, and the tube 2 a current of air is passed beneath the grid, 4, until the coal glows well and the air gas escapes by the chimney, *b*. By means of the handwheel, 14, the orifice, 5, and the valve 3 are closed, the motor of the fan, 1, being stopped and the steam cock, 10, and the valve 9 opened so that the steam enters at the top of the producer, *G*, while the water gas issues below the grid, 4, passes through the tubes 9 and *t*, and bubbles into the vessel 11, which collects the washing and cooling water from the scrubber filled with coke. The water discharges at the hydraulic seal, *A*, and the washed water gas passes from the top of the scrubber through the tube 12 to the gasometer. Meanwhile the temperature of the coke in the generator has been lowered; by the handwheel, 14, the valve 9 and the steam in 10 are shut off and the communications established as in the first phase to invigorate the combustion with air from the fan, this being injected under the grid, 4; this third phase is followed by the fourth, in which water gas is produced, the steam now being passed in from beneath the grid by means of the tube 10′. Thus the steam enters once at the top and once at the bottom.

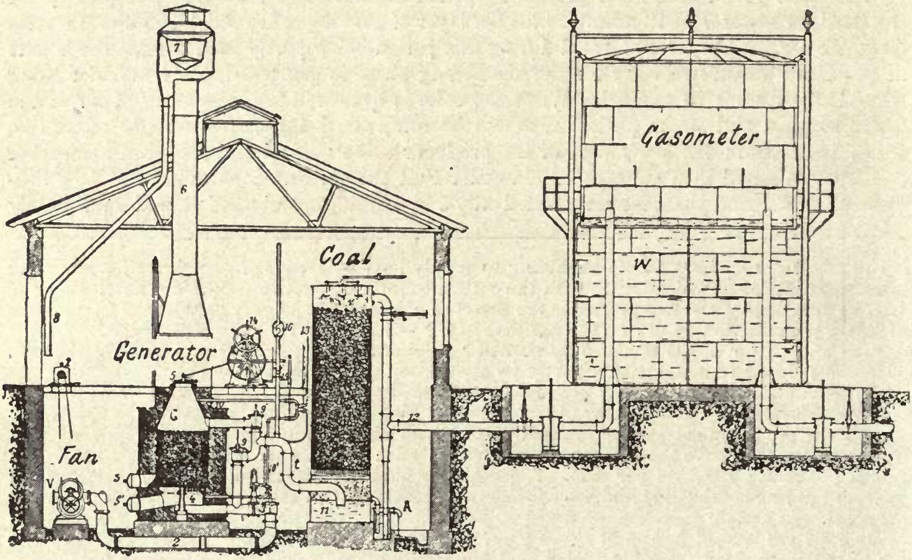


FIG. 197.

Every four or six phases coke is added at the top by means of the aperture 5 and the ash and slag are discharged from the lateral orifices of the producer (*S* and *S′*), which then close hermetically. The fumes issue from the catch-funnel, 7, which retains the coke dust carried over by the air current and passes it down the tube 8 to be collected. If an excess of oxygen is used, the carbon gives CO_2 in preference to CO even above 1000°, so that care must be taken not to mix the water gas with air gas, which is of less value and may form a detonating mixture in the gasometer. Fig. 198 shows a view of a small producer.

One kilo of coke containing 90 per cent. of carbon produces up to 2·5 cu. metres of water gas; 1 kilo of ordinary coal produces about 2 cu. metres, and 1 kilo of lignite 1 cu. metre. Crude water gas from coke contains 45 to 50 per cent. by volume of H, 38 to 45 per cent. of CO, 4 to 7 per cent. of CO_2, 4 to 5 per cent. of N, and about 1 per cent.

of oxygen; the calorific power is about 2500 cals. per cubic metre, and the gas costs from 0·3*d.* to 0·5*d.* per cubic metre.

As a rule water gas is used without further purification, especially when it is used for heating purposes; when, however, it is employed in gas engines, it is advisable to purify it from sulphur compounds by passing it through layers of hydrated ferric oxide, just as in the case of illuminating gas (*see* Vol. II., "Organic Chemistry").

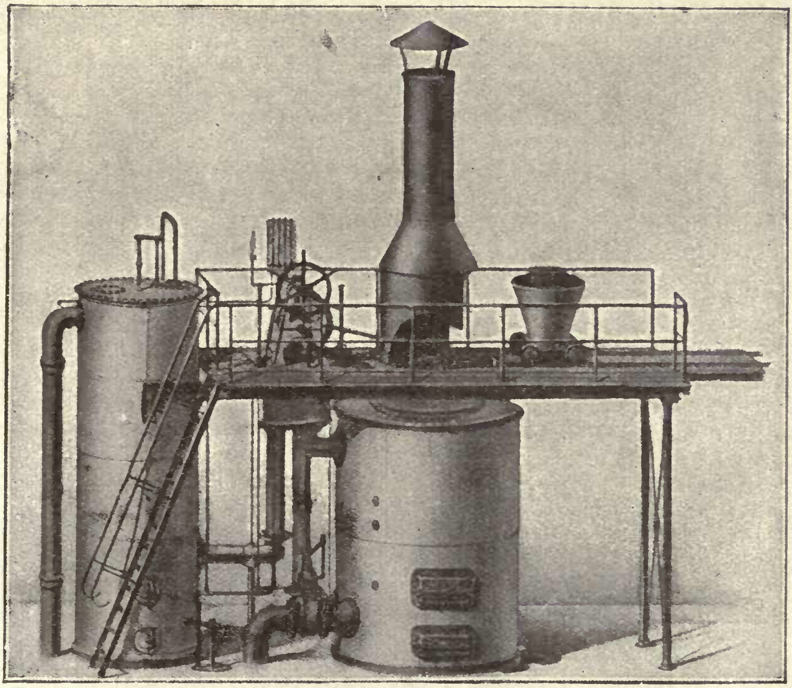


Fig. 198.

For complete combustion:

1 cu. metre of illuminating gas of 4590 cals. requires 5·21 cu. metres of air, and 1 cu. metre of the mixture has a calorific value of 736 cals.

1 cu. metre of water gas of 2300 cals. requires 2·15 cu. metres of air, and 1 cu. metre of the mixture has the calorific value 730 cals.

1 cu. metre of suction gas of 1095 cals. requires 1 cu. metre of air, and 1 cu. metre of the mixture has the calorific value 550 cals.

1 cu. metre of blast furnace gas of 883 cals. requires 0·75 cu. metre of air, and 1 cu. metre of the mixture has the calorific value 500 cals.

Although its calorific value is less than that of illuminating gas (5000 cals.), good water gas (2600 cals.) is capable of giving a higher temperature, since it burns with a smaller quantity of air and the quantity of combusted gases to be heated is thus less. For this reason, water gas may be used advantageously and economically in place of the oxy-hydrogen or oxy-acetylene blowpipe in the autogenous welding of sheet iron for boilers, tanks, etc. It is used also in autogenously welding large wrought-iron plates into piping for aqueducts capable of withstanding high pressures.

PRODUCER GAS. In certain cases *producer gas* (air gas, Siemens gas, or generator gas) is used for heating and power. It is prepared by passing a current of air, together with a very small spray of water, over an excess of red-hot carbon in such a manner that a gas containing about 28 to 33 per cent. of carbon monoxide, very little hydrogen (1·5 to 4 per cent.), 0·8 to 4 per cent. of CO_2, and 62 to 64 per cent. of N is obtained.[1]

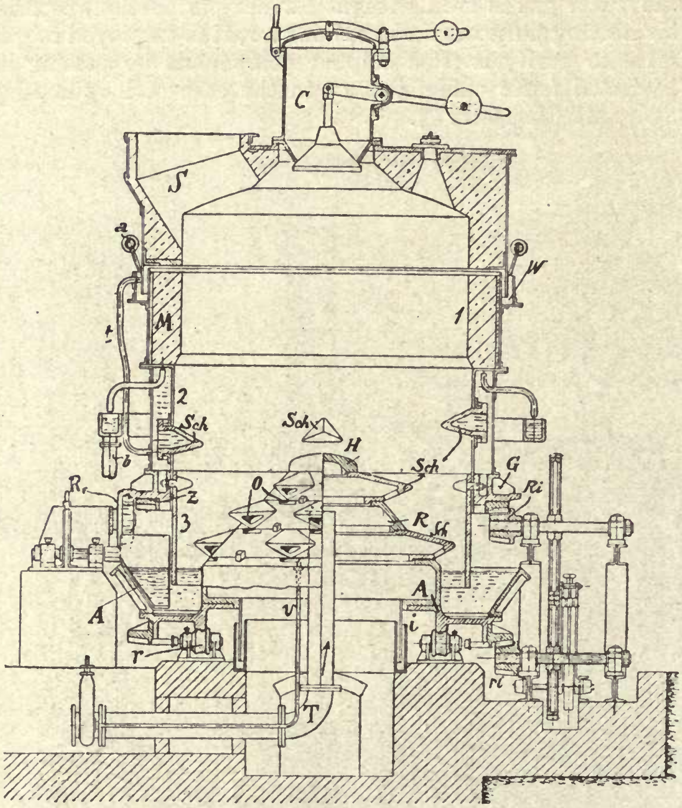


Fig. 199.

Finally *suction gas* or *Dowson gas* may be prepared, this having a composition intermediate to those of the two gases last referred to—about 25 to 30 per cent. of carbon

---

[1] **Producer Gas.** If the coal or coke were gasified with the theoretical quantity of air ($2C + O_2 = 2CO$), the ideal air gas obtained would contain only CO and N in the proportions, 34·7 and 65·3 per cent. respectively. Since each mol. of oxygen gives two mols. of CO (twice the volume), 100 vols. of air containing 21 vols. of O_2 and 79 of N_2 yield 42 vols. of CO and 79 of N_2, making a total of 121 vols.; the percentages by volume are thus 34·7 and 65·3 respectively. The weight of 1 litre of CO is 1·251 grms., so that the 347 litres of CO in 1 cu. metre of ideal air gas will weigh 434 grms. and the calorific value of 1 cu. metre will be 2420 × 434 = 1050 Cals. One kilo of coke may give about 6 cu. metres of air gas with a calorific value of 810 cals. per cu. metre, *i. e.*, 4860 cals. in all, and 1 kilo of ordinary coal may give 4·5 cu. metres of a gas which contains as much as 6 per cent. H_2 and 2 per cent. CH_4 and only 62 per cent. N_2 and a calorific value of 1070 cals., *i. e.*, 4815 cals. in all; the heat of direct combustion of the coal is 7500 to 8000 cals., part of this being lost with the flue gases and with the excess of air (50 to 100 per cent. more than the theoretical amount) required to burn the coal completely in ordinary furnaces; this loss is about 2000 cals.

The use of gaseous fuel (producer gas, water gas, etc.), presents, however, the following advantages: (1) The combustion is more easily regulated, the excess of air used being not more than 25 per cent., so that less heat is lost in the flue gases. (2) The latter may be utilised for heating, the use of a fan to draw them into the economiser being without influence on the course of the combustion. (3) The combustion may be carried out with hot air in order to obtain higher temperatures. (4) A non-smoky flame is obtained, that formed by the combustion of coal containing unburnt carbon. (5) Oxidising or reducing combustion may easily be produced as required. (6) Very high temperatures (gas retorts, glass furnaces, Martin-Siemens furnaces, zinc burners, porcelain furnaces, etc.), are best obtained with gaseous fuel, especially water gas.

monoxide, 12 to 18 per cent. of hydrogen, 4 to 5 per cent. of carbon dioxide, and 50 to 55 per cent. of nitrogen. It is obtained by passing a current of superheated steam, together with air, over red-hot carbon.[1] *Mond gas* is, in general, obtained from peat, etc. (*see* p. 363).

---

[1] This procedure yields a gas consisting of three-fourths of air gas and one-fourth of water gas, so that the calorific value is about 1300 cals. per cu. metre. It is the most convenient gas for engines, especially as the brothers Körting, by means of a simple aspirating device, have succeeded in feeding the engines with the gas direct from the producers, which are also fed synchronously with air and steam; collection of the gas in gas-holders is thus avoided. In order that dust and tar may not be introduced into the engines, it is preferable to use coke or anthracite in the generators; with suitable purifiers, however, coal, lignite, and even peat have been employed. Suction gas costs, according to the price of coal, 0·1 to 0·2*d*. per cu. metre.

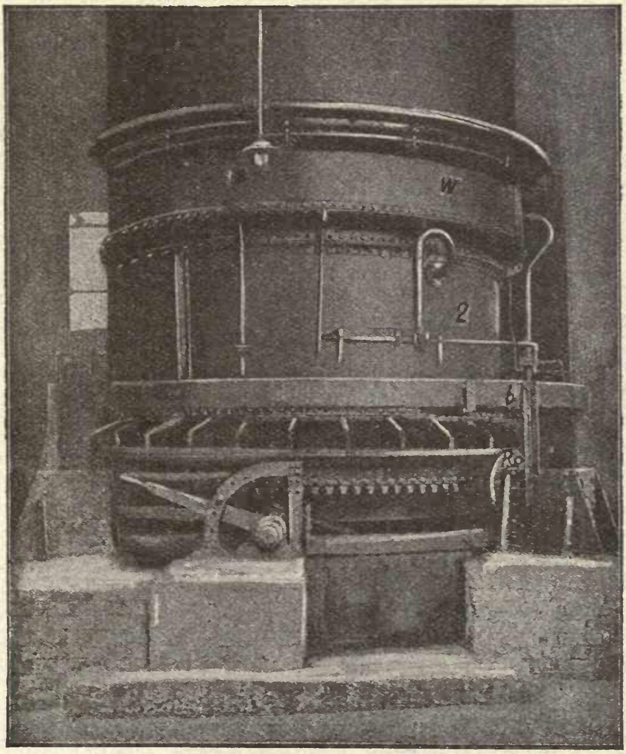


Fig. 200.

The main advantages of the gasification of fuel in comparison with its direct combustion are: easy and rational regulation of the combustion, elimination of smoke and the consequent losses, and the possibility of attaining very high temperatures. Good generators were formerly lacking, but excellent results are obtained nowadays, particularly with the Golia rotating-hearth generator made by Messrs. Küpper (Ger. Pat. 210,889), these admitting of the direct gasification of ordinary coal even if this agglomerates readily owing to excessive ash. Usually CO_2 is first formed, this being reduced by carbon above 1000° to CO, but if the temperature reaches 1400° or more, a semi-fused mass of slag and coal is formed which may block the hearth. The proper quantity of coal being used, the temperature is regulated between 1200° and 1400°. Since the carbon dioxide should be distributed uniformly across the zone of glowing carbon and should not pass through channels formed in the mass, generators with revolving hearth or revolving body have been devised to give homogeneous distribution of the CO_2 as it is formed, without incrustation of the slag. Figures 199 and 200 represent section and general view of a small generator of this type, having a diameter less than 3 metres and able to gasify 30 tons of coal, even when partly dust. Not only is the hearth rotatable, but part of the body of the generator revolves in the opposite sense. The body consists of three sheet-iron cylinders, 1 being coated inside with refractory material, *M*, 2 having double walls cooled by circulating water, and 3, of simple sheet-iron, making a hydraulic seal with the water of the ash pan, *A*, which is moved in the opposite direction by the gear wheels, *ri*, whereas the wheels *Ri* rotate the body of the generator. The cupola of the generator with the charging hopper for the coal, *C*, and the outlet

Mention has been made of these gases because they have effected a revolution in the production of energy, and in many cases they advantageously displace steam-engines in countries where fuel is dear, as in Italy.

Reference may also be made to another gas which is obtained during the dry distillation of wood (*Riché gas*). This industry cannot be carried on unless the secondary products which result, namely, methyl alcohol, acetic acid, tar, wood charcoal, etc. (*see* Vol. II., "Organic Chemistry"), are rationally utilised. Riché gas is of varying composition, but often contains about 60 per cent. of CO_2, 25 per cent. of CO, 15 per cent. of methane, and a very small quantity of hydrogen.

All these gases are employed as a source of power by means of gas engines. The cost of a h.p.-hour obtained from them varies greatly, according to the size of the engine, and may be from 0·15*d*. to 0·4*d*., whilst an electric h.p.-hour costs from 0·3*d*. to 1·2*d*., according to the locality, and a h.p.-hour obtained by steam costs from 0·8*d*. to 1·5*d*. and even more, according to the size of the boiler and steam-engine. A h.p.-hour can sometimes be produced from 800 litres of good water gas, but in the case of certain other gases 3 cu. metres are required. The calorific intensity of producer gas is sometimes as low as 850 cals. per cu. metre, but may reach 1100 cals.

When water gas is carburetted with benzene, etc., its calorific power rises to 5000 cals., and it may be advantageously mixed with illuminating gas.

CARBON SUBOXIDE : C_3O_2, the constitution of which is probably : $OC:C:CO$, was first obtained by Diels and Wolf in 1906 by decomposing ethyl malonate, and later in 1908 from malonyl chloride. It is a gas of disagreeable odour, which liquefies at + 7°. When heated with oxygen it yields CO_2. With cold water it forms malonic acid :

$$C_3O_2 + 2H_2O = CH_2(COOH)_2.$$

It reacts with NH_3 and aniline even below 0°, and also reacts with gaseous HCl. When liquid, it is transformed in a few days into an amorphous blackish-red solid mass which liberates a quantity of carbon monoxide at 37°. Berthelot appears to have obtained an oxide, C_4O_3, in 1876.

NICKEL TETRACARBONYL : $Ni(CO)_4$. This compound was obtained by L. Mond in 1890 by the action of CO on finely divided nickel at a temperature of 25° to 30°. The CO acts as a divalent residue, called *carbonyl*. Nickel tetracarbonyl is a colourless liquid, very refractive to light. It boils at 43° at a pressure of 751 mm. and crystallises at − 25°. Its vapours decompose at 60° with explosion. Iron *carbonyls*, $Fe(CO)_4$ and $Fe(CO)_5$, are also known.

CARBONYL CHLORIDE : $COCl_2$ (phosgene or carbon oxychloride). As seen with the preceding compound the radical CO has free carbon valencies, and these may be saturated also by chlorine. Carbonyl chloride is obtained by the direct action of sunlight on a

---

for the gas are fixed. The cupola and the revolving body are sealed hydraulically by means of the small sleeve, *W*, through which there circulates water which is discharged from the tube *t* and goes to cool the ring 2 and collects in the circular channel, *b*. In the interior of the ring 2 are inserted cutting teeth, *Sch*, which are also water-cooled and serve to prevent the formation and deposition of slag. The revolving body of the generator is fixed to a stout cast-iron ring, *Z*, which rests on four rollers, *Ro*, with their outer edges raised to centre the whole of the revolving body. The hearth is formed from a stout cast-iron truncated cone, *ARH*, fixed to the large cast-iron basin, *A*, which is filled with water to collect the ashes, rests on the rollers *r*, and is moved by the gearing, *ri*. Teeth, *Sch*, are also fixed to the conical hearth, these carrying fissures, *O*, for the entry of air from *T* or steam from *v*; the empty inner part of the cone is sealed hydraulically by a tall ring, *i*, which holds the pressure of the gases (the air is injected at a pressure of 90 to 110 mm. and the gas issues at 40 mm.). The ashes obtained with regular working contain less than 0·5 per cent. of combustible matter. The calorific value of the gas is more than 1400 cals. per cu. metre for the composition : 2·5 to 3·5 per cent. CO_2, 0·1 to 0·3 per cent. O, 54 to 56 per cent. N, 10 to 11 per cent. H, 26 to 28 per cent. CO, 1·7 to 2 per cent. CH_4 and 0·2 to 0·5 per cent. of unsaturated hydrocarbons; every cu. metre contains only 20 grms. of moisture, so that water gas can be produced without excess of steam. The ashes are removed automatically and continuously from the pan. The rate of turning is very small, being only 4 to 5 revolutions per twenty-four hours, the consumption of power being 2·5 h.p. Such producers exhibit appreciable advantages for the heating of Martin furnaces for making iron and steel.

mixture of carbon monoxide and chlorine: 1 vol. CO + 1 vol. Cl_2 = 1 vol. $COCl_2$; it is also obtained by passing this gaseous mixture over red-hot spongy platinum, or more easily over powdered vegetable or animal charcoal (Paternò, 1878), an excess of CO being used. This process was used in large dye factories and in 1916 Helbig improved it by using as catalyst a very active carbon prepared by powdering highly purified animal charcoal, subjecting it to special treatment and then compressing it into cakes, which become very porous when heated in covered crucibles or retorts. Helbig prepared pure carbon monoxide by passing pure CO_2 (from cylinders of the liquefied gas) through a special coke furnace heated electrically so as to obtain a uniform temperature throughout the whole mass. The CO collected in the gasometer is passed into a tube together with an almost equal volume of chlorine (analysed frequently to ascertain how much air it contains) and the mixture passed through the catalyst, which should be cooled to some extent to prevent the temperature from exceeding 250° (the reaction being exothermic). If the phosgene is to be used for charging asphyxiating bombs, it is previously liquefied by cooling to — 35°. In Vitali's factory at Rumianca (Novara) Helbig produced in 1917 as much as 4000 kilos of liquid phosgene per day, and in 1918 the output was raised to 6000 kilos per day, the yield being 75 to 85 per cent. Phosgene may also be obtained from CO and $SbCl_5$, since in the hot two atoms of chlorine are liberated from the salt and react with the carbon monoxide: $CO + SbCl_5 = SbCl_3 + COCl_2$. It has also been prepared by the Michalski process (U.S. Pat. 808,100, 1906), in which a mixture of quicklime, calcium chloride, and powdered coke is heated in the electric furnace: calcium carbide remains, while phosgene is evolved.

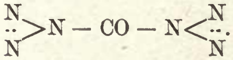
During the European War it was made in various countries by the uneconomical but easy process of heating fuming sulphuric acid (60 to 80 per cent. of free SO_3) at 100° in an iron vessel fitted with a reflux condenser, through which carbon tetrachloride is introduced; the phosgene evolved is dried with sulphuric acid and liquefied by cooling: $CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2$ (pyrosulphuryl chloride, used in the manufacture of saccharin: *see* Vol. II., "Organic Chemistry"). The yield may reach 85 to 90 per cent., but the product is much dearer than that made from CO and Cl_2.

It is a colourless, suffocating gas of sp. gr. 3·5 and at 7° it is converted into a liquid of sp. gr. 1·432; the gas is soluble in benzene or acetic acid. By water, especially in the hot, or better by steam, it is readily decomposed: $COCl_2 + H_2O = 2HCl + CO_2$.

It is used industrially for the manufacture of various organic products, *e. g.*, diphenylurea (*see* Vol. II.)—from diphenylamine and phosgene—but serves mostly for making dyes derived from di- and tri-phenylmethane. In small quantities it used to be sold in steel cylinders at £1 8*s.* per kilo, but when made in thousands of tons as a poison gas during the European War its price fell considerably (in Italy the Government paid 6*s.*, and sometimes as much as 12*s.* per kilo for that made from CCl_4 and only 2*s.* for the Helbig product).

As a poison gas it is more harmful than chlorine, since it has fatal effects even when largely diluted with air (0·025 per cent.), and these effects are sometimes produced after twenty-four or thirty-six hours. The masks used by the soldiers as a protection against phosgene consisted of sponge soaked in sodium sulphophenate and sodium carbonate (Ciamician). It is also fixed by resorcinol (and phenols in general), and, quantitatively, especially in presence of sodium carbonate.

CARBONYL NITRIDE: $CO(N_3)_2$. This compound was prepared by Curtius in 1894, and is formed of divalent carbonyl saturated with two residues of hydrazoic acid:



$\begin{matrix}N\\ \cdot\cdot\\ N\end{matrix}\!>N - CO - N<\!\begin{matrix}N\\ \cdot\cdot\\ N\end{matrix}$. It is a crystalline substance which is very volatile and somewhat explosive.

CARBON DISULPHIDE: CS_2

This compound is formed by the action of sulphur vapour on red-hot carbon, the vapours of carbon disulphide being then condensed to form a liquid which when pure is almost colourless, has a special odour, and is very mobile and refractive. It has a specific gravity of 1·262 at 20°, and boils at 46·5°. It is insoluble in water, but dissolves in all proportions in alcohol and ether and is also soluble in oil to the extent of 60 per cent. It is an endothermic compound:

$C + S_2 = CS_2 - 5{\cdot}3$ Kj., and is therefore formed only on heating. It easily catches fire and burns with a bluish flame:

$$1 \text{ vol. } CS_2 \text{ (vapour)} + 3 \text{ vol. } O_2 = 1 \text{ vol. } CO_2 + 2 \text{ vol. } SO_2.$$

The vapour of CS_2 also burns in an atmosphere of nitric oxide with an intense bluish-white flame very rich in actinic rays. It is a very good solvent for iodine (with which it gives a violet solution), sulphur, phosphorus, and rubber, and also for many fats. Carbon disulphide vapour is harmful to the system, and often produces fatal poisoning if inspired.

INDUSTRIAL MANUFACTURE. In certain localities iron, zinc, or antimony sulphides are mixed with carbon and heated, but the largest quantities of carbon disulphide are prepared by heating sulphur directly with carbon. The first important industrial plant was devised by Deiss, and whilst CS_2 still cost £2 per kilo in 1840, in 1848 Deiss prepared it at 6*s.* 4*d.* per kilo, and the price descended later to 5*d.* per kilo. Deiss's apparatus has been often modified, and the arrangement most used to-day is that of Singer (Fig. 201): A cast-iron retort, *A*, 1·7 metres high, the walls of which are 5 to 7½ cm. thick, is filled with gas coke or beechwood charcoal, and heated in a furnace with double walls,[1] between which the furnace gases circulate.

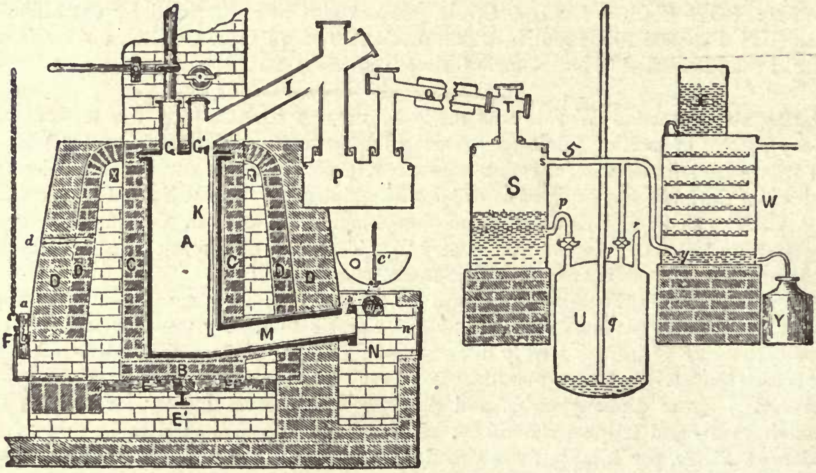


FIG. 201.

The sulphur is melted apart in the pan, *c'*, and is allowed to drop slowly into the lower tube, *M*, of the retort. It then evaporates and passes through the carbon which is heated to dull redness, forming vapour of carbon disulphide mixed with sulphur vapour and a few other impurities, such as CO_2, H_2S, etc. In the delivery tube, *I*, which is slightly inclined, a great part of the sulphur condenses and runs back to the bottom of the retort through the tube *K*. The remaining sulphur vapours are deposited and condensed in the vessel *P*.

The carbon disulphide vapours are condensed, on the other hand, in a condenser, *Q*, which is about 9 metres long, and round which cold water passes. The liquid CS_2 accumulates in the vessel *S* and passes continuously into the reservoir, *U*, from which it is forced by air pressure into large settling tanks. The miscellaneous gases, especially H_2S, which are mixed with the CS_2, are not condensed in the vessel *S*, but bubble through the tube *sy* into oil, which extracts the remaining CS_2 vapours. They then pass through the purifier, *W*, consisting of several trays over which runs oil from the tank, *x*. This oil removes the last traces of CS_2, and is collected in the reservoir, *Y*. The gases which escape from the purifier are then passed through solutions of alkali or ferrous sulphate in order to

---

[1] The walls of the retort are made so thick because the iron undergoes partial attack. It is found that in a retort weighing 1500 kilos 20 tons of CS_2 may be produced. If, however, the furnace is badly constructed or the cast-iron of the retort is of poor quality, it may become corroded in a few days. Retorts weighing 4 tons last six or seven weeks.

absorb the H_2S. Laming's material may also be used for this purpose as in gas-works. Various more perfect systems of condensation for the CS_2 vapours have been proposed and these reduce the losses to a minimum.

If the operation is well conducted 90 per cent. of the sulphur is transformed into CS_2.

The crude carbon disulphide contains in solution 8 to 10 per cent. of sulphur and certain gaseous impurities which are not separated by direct distillation. It is, therefore, first shaken with lime water and then placed in a still together with 1 per cent. of oil, a little water, and a little lead acetate. It is then distilled from a water-bath. Fairly pure CS_2 is thus obtained and may be further purified by distillation.

In America much carbon disulphide is to-day prepared by the Taylor process (U.S. Pats. 688,364 of 1901 and 871,971 of 1907, and Ger. Pat. 706,128 of 1902) in a special electric furnace in which the carbon and sulphur are heated to high temperatures. These furnaces have been constructed to yield 12 tons of carbon disulphide per twenty-four hours, using 400 h.p., and the most suitable form has been shown to be that of very large diameter—more than 4 metres for a height of 12·5 metres. Further, it is better to use wood charcoal in place of the coke formerly employed. Small furnaces give bad yields and are worn out more easily by the high temperatures. The Taylor furnace shown in Fig. 202 is too high in relation to the diameter. Sulphur is introduced at *NS* to the level of the electrodes, wood charcoal being introduced at *CK* and used to fill the chimney of the furnace, *F*. Four graphite electrodes, *D*, joined outside by aluminium rods and traversed by a biphase current, are used. Economy in electrodes is effected by the continuous introduction into the hot zone of pieces of charcoal, which are dropped down the channels *CK*. The temperature inside the furnace varies from 550° to 850°. In the zone where the fused sulphur is surrounded by the arc, carbon disulphide is formed continuously, its vapour passing through the charcoal in the chimney, *F*, before it proceeds through the tube *P* to the condensing plant.

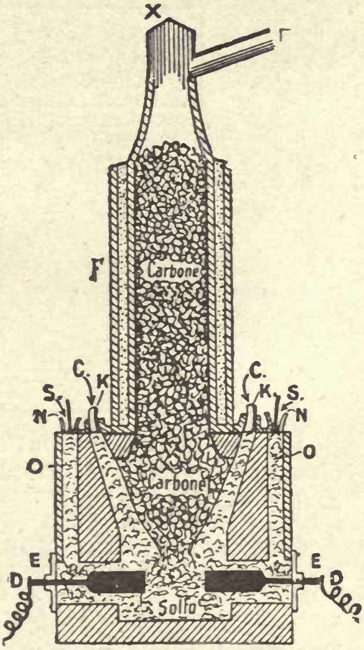


FIG. 202.

USES OF CS_2. Until 1850 this substance was employed industrially only for vulcanising and dissolving rubber, but its use as a solvent has now greatly extended in many industries. Attempts have been made to use it for the extraction of sulphur from poor ores. It is used for extracting aromatic oils from drugs, and in large quantities for the extraction of oil from seeds and oil seed residues (for apparatus *see* Vol. II., " Organic Chemistry "). It is used also for degreasing vegetable and animal residues, such as rags, bones, meat, hides, wool, etc. It is used for preparing solutions of wax for coating plaster casts and for the preparation of waxed paper. It is also used for dissolving out the tar from many industrial by-products, for preparing various chemical products, for making Greek fire (phosphorus dissolved in CS_2), for killing insect pests, and, more especially, in large quantities for destroying phylloxera in vineyards by injecting it into four or five holes per sq. metre of soil (about 50 grms. per cu. metre; treble this dose injures the roots of some plants a little). Owing to its volatility, large quantities are, however, lost in this way, even when it is used dissolved in water (0·5 per cent.). Nowadays it is advantageously replaced almost everywhere by potassium trithiocarbonate (*see* Part III.). In 1910 2250 communes in Italy were invaded by phylloxera over an area of 450,000 hectares. In 1906 it was used with good results for destroying the nematodes which attack beetroot. Since 1910 the consumption of carbon disulphide has been rapidly increasing owing to its use in the manufacture of artificial viscose silk (*see* "Organic Chemistry"); in Italy the only viscose factory, at Pavia, uses about 200 tons per annum (*i. e.*, about 1 kilo per kilo of silk produced).

In France about 550 tons were produced in 1900, and in Germany about 650 tons; Hungary produced 2760 tons in 1905.

The Italian output and exportation were as follows:

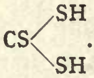
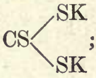
Year	Production		Exportation	
	Tons	Value	Tons	Value
		£		£
1903	2000	22,760	300	—
1905	2306	27,600	—	—
1907	3560	—	782	—
1908	—	—	1075	—
1910	2225	29,910	1060	—
1911	2500	28,800	823	9880
1913	—	—	864	—
1914	2550	31,200	669	—
1915	3160	44,640	549	—
1916	—	—	369	5610

Its market price is about £16 per ton, although during certain years it was often sold at £12. It is placed on the market in sheet-iron vessels and is carried as inflammable goods.

CARBON MONOSULPHIDE, CS, was prepared by Dewar and Jones in 1910 by acting on nickel tetracarbonyl with thiophosgene in the cold:

$$CSCl_2 + Ni(CO)_4 = NiCl_2 + 4CO + CS.$$

This sulphide polymerises to an amorphous blackish-brown mass, which dissolves slightly in phenol and in carbon disulphide with a dark coloration. It has a specific gravity of 1·6, is unchanged at 360°, and forms CS_2 and carbon at a red heat. It dissolves in strong sulphuric acid to a purple solution and is regenerated unchanged on dilution with water. It dissolves also in alkalis and is re-formed on addition of acids.

TRITHIOCARBONIC ACID:  $CS\langle{}^{SH}_{SH}$. This compound is easily obtained in the form of potassium trithiocarbonate, by dissolving potassium sulphide in carbon disulphide, $CS_2 + K_2S =$  $CS\langle{}^{SK}_{SK}$; this salt is used for destroying phylloxera (*see* Part III., Potassium Salts). The acid is liberated by HCl and forms a reddish-brown and somewhat unstable oil. It may be considered to be derived from carbonic acid in which all the oxygen is replaced by sulphur.

CARBON OXYSULPHIDE: COS. This compound is obtained in small quantities by passing a current of sulphur vapour and CO through a red-hot tube. It is prepared more easily by the action of dilute sulphuric acid on potassium thiocyanate, CNSK. It is a colourless gas of similar odour to hydrogen sulphide and is found free in certain sulphuretted waters. It dissolves in an equal volume of water and slowly decomposes: $COS + H_2O = CO_2 + SH_2$. It burns easily, forming SO_2 and CO_2.

CYANOGEN COMPOUNDS. These are compounds of carbon with nitrogen which are always formed when nitrogenous organic compounds are heated with potassium hydroxide.

Potassium cyanide, KCN, is first obtained, and from this potassium ferrocyanide, $K_4Fe(CN)_6$ (yellow potassium prussiate), is formed with ferrous oxide.

All these cyanogen compounds contain the characteristic CN group, called *cyanogen*, which acts as a monovalent radical. From potassium cyanide and ferrocyanide all the numerous other cyanogen compounds, which are studied in Vol. II., " Organic Chemistry," are formed.

HYDROCYANIC ACID : HCN (prussic acid) is the acid corresponding with potassium cyanide. It is a colourless liquid which boils at 27°, and is obtained by distilling a concentrated solution of potassium cyanide or ferrocyanide with dilute sulphuric acid (with strong sulphuric acid CO would be formed). HCN is an endothermic compound. According to W. Feld (Ger. Pat. 217,272, 1908) the yield is improved if the cyanide or ferrocyanide solution is replaced by the powdered salt and if the latter is treated with sulphuric acid, and, when the mass is hot, steam is passed so that water does not condense on the reacting mass; alternatively, the cyanides may be mixed with salts which liberate water vapour in the hot.

According to U.S. Pat. 967,943 of 1910, an almost theoretical yield of hydrocyanic acid is obtained by passing a mixture of trimethylamine and ammonia into a red-hot tube: $N(CH_3)_3 + 2NH_3 = 12H + 3HCN$.

Mascicki (1909) and Lipinski (1911) prepare HCN on an industrial scale by passing a mixture containing, for instance, 20 per cent. CH_4, 10 per cent. H_2, and 70 per cent. N_2, into a high tension arc furnace, the whole of the CH_4 being used up if separation of lamp-black is avoided; the energy consumed is 1 kilowatt-hour per 23 grms. of prussic acid. With the exception of the ferrocyanides, which are not poisonous, both hydrocyanic acid and its salts are very powerful poisons; against the acid, 20 per cent. ferrous sulphate solution or powdered calcined magnesia acts as an antidote.

Other cyanogen compounds are described in the chapter on Iron and still others among the organic compounds (*see* Vol. II.).

SILICON: Si, 28.3

This element was prepared free in the amorphous state by Berzelius in 1823, by heating potassium fluosilicate with metallic potassium:

$$SiF_6K_2 + 4K = 6FK + Si.$$

Saint-Claire Deville obtained it in the crystalline condition by heating sodium fluosilicate with aluminium or with sodium and zinc; when powdered SiO_2 is heated with magnesium powder and the excess of Mg then dissolved in acid, silicon is obtained as a light-brown powder which is inflammable in the air. It is now prepared in considerable quantity in the electric furnace by reducing quartz with wood charcoal with addition of CaO and Mn_3O_4; the crude silicon which results is purified with HCl and HF and contains 90 to 91 per cent. of Si, 6 to 7 per cent. of Fe, 0·08 per cent. of Mn, about 2 per cent. of Al, 0·02 per cent. of P, and about 0·2 per cent. of carbon; the material so obtained is utilised in metallurgy to obtain iron which is hard and resistant to acids (ferrosilicon, etc.). The crystals obtained by this process are lustrous, black and hard, and form octahedra. They are separated from the fused zinc in which they are imbedded by dissolving the metal in HCl. Italy produced 629 tons of silicon (£23,505) in 1915 and 342 tons (£13,350) in 1916.

Silicon is one of the most abundant elements in nature,[1] and in combination with oxygen forms silica (silicic anhydride) SiO_2, as quartz, amethyst, agate, opal, various sands, etc. In the form of silicates it is the principal constituent of the more important rocks, especially of the primitive rocks (*see also* Kaolin, Clay, Mica, etc.).

Silicon does not exist free in nature and is obtained by heating silicon fluoride with sodium: $SiF_4 + 4Na = 4FNa + Si$; sodium fluoride is soluble

---

[1] It has been calculated that one-fourth by weight of the earth's crust consists of silicon, whereas oxygen forms 50 per cent. of the whole globe, including the atmosphere. The other elements are far less abundant, iron being present to the extent of 5 per cent. and carbon of 0·2 per cent.

in water and silicon results as a greyish-brown amorphous insoluble powder. According to Winkler it may be obtained pure by heating powdered quartz with powdered magnesium : $SiO_2 + 2Mg = 2MgO + Si$.

Free silicon formed by the reduction of silica by carbon is often found in cast-iron from the blast furnaces. Amorphous silicon is soluble only in HF (with evolution of H) or in alkalis. It does not conduct electricity, and forms SiO_2 when burnt in the air. Crystallised silicon is, on the other hand, a good conductor of electricity and is harder than glass. Its specific gravity is 2·49; it does not dissolve in any one acid, but only in a mixture of HNO_3 and HF, and does not oxidise, even when heated to redness in an atmosphere of oxygen. When boiled with a solution of sodium hydroxide it is dissolved with development of hydrogen, forming sodium silicate : $Si + 4NaOH = SiO_4Na_4 + 2H_2$. It melts at 1430°.

After being heated to high temperatures amorphous silicon behaves in the same manner as crystallised silicon, perhaps because it partially melts and becomes crystalline. When burnt in an atmosphere of dry chlorine, silicon forms silicon chloride, $SiCl_4$; if the chlorine is moist a portion of it is converted into SiO_2; with gaseous HCl at high temperatures it also forms $SiCl_4$, but some *silicochloroform*, $SiHCl_3$, is formed at the same time. It combines with fluorine in the cold, and even with nitrogen at high temperatures. In the electric furnace it combines with various metals forming *silicides*.

SILICON COMPOUNDS

SILICON HYDRIDE : SiH_4 (Silicomethane). This compound is formed on dissolving in hydrochloric acid an alloy of magnesium and silicon, obtained by heating 1 part of powdered quartz with 1·5 parts of magnesium powder. Thus the gas is obtained in an analogous manner to AsH_3 or SbH_3, which is obtained from an alloy of As or Sb by the action of zinc :

$$Si + Mg_2 + 4HCl = SiH_4 + 2MgCl_2.$$

Silicon hydride is evolved mixed with hydrogen and catches fire in the air because it contains small traces of silicoethane, Si_2H_6, and forms H_2O and SiO_2 in the form of smoke-rings in the same manner as PH_3. It is also obtained by the electrolysis of various chlorides, an aluminium cathode containing silicon being employed. It may be obtained free from hydrogen from various organic silicon compounds, for example, by heating the triethyl ester of silicoformic acid, $SiH(OC_2H_5)_3$, and then catches fire only on heating. It is a colourless gas of unpleasant odour and liquefies at − 1° under 100 atmos. pressure. It combines with chlorine with formation of flame. If it is passed into a glass tube and ignited at the end, a brown spot of amorphous silicon is obtained on introducing a cold porcelain surface into the flame; also if the glass tube is heated at any point a brown mirror of silicon is obtained analogous to that obtained with As and Sb, showing the ease with which it is decomposed into Si and H_4. With solutions of alkali hydroxides it forms alkali silicates :

$$SiH_4 + 2NaOH + H_2O = 4H_2 + SiO_3Na_2.$$

SILICON TETRACHLORIDE : $SiCl_4$. This compound is obtained on passing a current of dry chlorine over silicon and heating to 300°, or over magnesium silicide, or more easily over a red-hot mixture of SiO_2 and carbon : $SiO_2 + 2C + 2Cl_2 = 2CO + SiCl_4$. A little **Silicon hexachloride**, Si_2Cl_6, is always formed at the same time.

Silicon chloride formed in this manner distils as a colourless liquid of sp. gr. 1·52; it boils at 59·5°. It fumes in the air and is easily decomposed by water into hydrochloric acid and silicic acid : $SiCl_4 + 4H_2O = SiO_4H_4 + 4HCl$, whilst the chlorides of carbon are stable in contact with water.

Since silicon chloride vaporises without alteration, the atomic weight of silicon may be deduced indirectly from its vapour density and percentage composition.

Silicon Oxychloride : Si_2OCl_6, that is, $Cl_3 \vdots Si \cdot O \cdot Si \vdots Cl_3$, is also known, and so is a compound analogous to chloroform, $CHCl_3$, namely, Silicochloroform, $SiHCl_3$, which is a liquid boiling at 34°, and is obtained by the action of silicon hydride on phosphorus (or antimony) pentachloride. It is also formed together with $SiCl_4$ on heating silicon with dry HCl. In contradistinction to ordinary chloroform it is decomposed by water.

Silicon Bromide and Iodide: $SiBr_4$; SiI_4. These substances are obtained in an analogous manner to the chloride and possess similar properties. The bromide is a colourless liquid; the iodide forms colourless octahedra. **Silicobromoform**, $SiHBr_3$, **Silico-iodoform**, $SiHI_3$, and **Silicon Hexaiodide**, Si_2I_6, are also known.

SILICON FLUORIDE: SiF_4, and **HYDROFLUOSILICIC ACID**: H_2SiF_6. The first compound is obtained on heating calcium fluoride mixed with silica or silicates (sand, powdered glass, etc.), with sulphuric acid; hydrofluoric acid is first formed and immediately reacts with the silica:

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

It is a colourless gas which fumes strongly in the air and has a pungent odour. It is liquid at − 160°, and does not attack glass when completely dry. It is formed in large quantities during the manufacture of superphosphates, and since it is harmful to respiration and to vegetation, especially to mulberry trees, these works to-day recover it all in the form of hydrofluosilicic acid (*see* Superphosphates, Part III). It is characterised by the fact that it is immediately decomposed by water, forming gelatinous silicic acid, H_4SiO_4, and hydrofluosilicic acid, H_2SiF_6, which remains dissolved in the water:

$$3SiF_4 + 4H_2O = SiO_4H_4 + 2H_2SiF_6.$$

In the laboratory preparation of hydrofluosilicic acid, the mixture of $CaF_2 + SiO_2 + H_2SO_4$ is heated in a flask, and the gaseous SiF_4 evolved is passed through a shallow layer of mercury at the bottom of a cylinder of water so that the gelatinous silicic acid which is formed cannot obstruct the delivery tube. The gelatinous silicic acid is then collected on a filter, the filtrate consisting of an aqueous solution of hydrofluosilicic acid, which cannot be separated unchanged because on evaporating the water SiF_4 escapes and a solution of HF remains. The aqueous solution of H_2SiF_6 behaves like a halogen acid. It dissolves the metals with evolution of hydrogen and forms salts with bases, behaving as a dibasic acid. Barium fluosilicate is insoluble in water. Potassium fluosilicate, K_2SiF_6, is soluble with difficulty, and the other fluosilicates are almost all soluble.

With a concentrated solution of HF silicon fluoride forms a *hydrate*, $H_2SiF_6 + 2H_2O$, which is obtained solid and melts at 19°.

Hydrofluosilicic acid does not attack glass and is used for hardening pastes of plaster of Paris or cement, perhaps because it forms calcium fluoride and separates SiO_2. It has a powerful antiseptic and anticryptogamic action, and is used for preserving wood and oil pigments.

Solutions of hydrofluosilicic acid of 20° Bé. cost about £18 per ton, and sodium fluosilicate costs about £26.

SILICON CARBIDE: SiC, ordinarily called **Carborundum**. This substance was accidentally obtained by Acheson whilst endeavouring under Edison's advice to prepare artificial diamond by dissolving carbon in fused aluminium silicate at very high temperatures in the electric furnace. He actually produced carbon silicide, which was studied in 1892–1894 by Mühlhäuser, who determined its composition. It is now known that the temperature of formation of carborundum is from 1920° to 1980° and that its decomposition into graphite and silicon (*see* p. 440) occurs at 2220°. It is to-day prepared in large electric furnaces from a mixture of 3 tons of powdered coke, 6 tons of siliceous sand, and 1·5 tons of sodium chloride which is used as a flux and may be partly replaced by sawdust to render the mass porous during the heating: $SiO_2 + 3C = 2CO + SiC$. The silica is then eliminated by means of a boiling mixture of nitric and hydrofluoric acids. A crystalline mass remains, of greenish-blue colour, which is extremely hard and is only slightly softer than diamond. The Carborundum Company at Niagara uses 10,000 electrical h.p. at 250 volts in 2000 h.p. furnaces, the material from the furnaces being ground by means of manganese steel grindstones, treated with sulphuric acid to remove the iron (or magnets are used), washed and dried.

As powder or suitably agglomerated it forms an excellent abrasive or grinding-wheel and advantageously replaces emery for polishing purposes, especially for metals.[1]

Scarcely any solvents dissolve it, but it is attacked by fused sodium hydroxide or sodium carbonate.

As it is very resistant to high temperatures and a better conductor of heat than many other substances, endeavours have been made to utilise it as a refractory material or for ingot moulds for molten aluminium, more especially as it is not altered by great variations of temperature. Since, however, it is still very dear, it is only used to-day in the form of a cement or varnish for coating ordinary refractory materials. Carborundum is used also for the refining and desulphuration of steel.

In 1905 Bölling prepared a product called *silundum* which is similar to carborundum and is used for the preparation of electrodes. It is formed of carbon which is combined with silicon vapour at a temperature of 1800° to 1900°. Thus on placing pieces of carbon shaped into any desired form in the electric furnace and covering them with silicon carbide and silica, at 1900° the silicon is transformed into vapour and penetrates all the pores of the carbon, combining with it and also depositing in it. A compact non-porous mass of suitable form results which conducts the electric current and transforms it into thermal energy at the highest temperatures, for which platinum can no longer be used. It offers greater resistance than carbon to the passage of the current. It may possibly be applied for electric heating for domestic purposes.

In 1903 the production of carborundum at Niagara was 2370 tons and in 1904 it rose to 3500 tons of the value of £140,000. In Italy in 1905, 850 tons were produced, and in 1906 about 1100 tons of the value of £13,520. In 1913 the Lonza Company in Switzerland produced more than 600 tons of silicon carbide. The total world's output in 1911 was 10,000 tons. The consumption in France in 1911 was estimated at about 60 tons.

Carborundum containing 68·3 per cent. of silicon costs about £64 per ton, and when powdered as much as 2*s.* per kilo or, for large quantities, 9½*d.* per kilo. When spread on sheets of paper it costs 7*s.* 2*d.* per 100 sheets and on sheets of linen 12*s.* 10*d.*

CALCIUM SILICIDE : $CaSi_2$, is used for reducing and desulphurising metals. It is obtained by heating in the electric furnace the following mixture: 64 parts of calcium carbide, 120 parts of silica, and 24 parts of coal: $CaC_2 + 2SiO_2 + 2C = 4CO + CaSi_2$ (Ger. Pat. 206,785).

IRON SILICIDE or **FERROSILICON.** *See* chapter on Iron.

---

[1] *Grindstones* were formerly made from natural abrasives (emery or corundum), but nowadays artificial products (carborundum, alundum) are mostly used. The best emerys (with 50 to 60 per cent. Al_2O_3) are obtained from the island of Naxos (Greece), Smyrna, and Chester (Massachusetts). Corundum contains 75 to 85 per cent. of Al_2O_3 and is found in Brazil, Georgia, and Western Ontario. The stones are formed by first mixing the powdered abrasive with a certain amount of dry clay and flux (as for earthenware), a little water being added, and when a homogeneous mass is obtained in the mixer, it is poured into moulds. Fine stones are allowed to dry in the air (to avoid cracking), whereas those of coarse grain are heated to 50° for 2 to 3 days in a ventilated room; they are then dusted over with powdered quartz and baked in furnaces at 1500°, as in the stoving of porcelain. The cooling is gradual and lasts 3 to 4 days, the surface of the stones being then made true by turning. Then come centring and tests of equilibrium and rotation with a peripheral velocity of 45 to 50 metres per second (in practice, this velocity is 25 metres per sec.). More perfect stones are those which are hydraulically pressed before baking instead of pouring into moulds.

The following are the physical constants of refractory materials. Thermal conductivity (gram-cals. per c.cm. per 1° per sec.): carborundum bricks, 0·0231; magnesia bricks, 0·0071; bricks of chrome residues, 0·0057; silica bricks, 0·0020; ordinary firebricks, 0·0042. The transmission of heat through carborundum bricks is 7 to 8 times as great as with ordinary refractory materials. The specific heat of carborundum is 0·19 and that of firebrick, 0·2243. The coefficient of expansion of carborundum between 200° and 900° is 0·0000047. Deformation or fusion is resisted up to 1200° for silica bricks, 1450° for chrome bricks, 1550° for magnesia bricks, and 1820° for those of carborundum. The specific gravity of carborundum is 3·2 and that of carborundum bricks 2·1 to 2·5. The Niagara Company sells two forms of carborundum refractories, known as Carbofrax and Refrax.

France imported 690 tons of powdered, and 998 tons of agglomerated emery in 1913, and 424 (42) tons of powdered and 641 (555) tons of agglomerated emery in 1914 (1915).

SILICON DIOXIDE : SiO_2 (SILICIC ANHYDRIDE, SILICA)

Until a short time ago this compound was the only one known of silicon and oxygen; now, however, a monoxide of silicon, SiO, has also been prepared. The dioxide is found abundantly in nature in the form of *quartz* or *rock crystal* and of *flint*. Quartz is often pure silicon dioxide and crystallises in hexagonal prisms and pyramids. It is generally almost colourless, but is called by different names according to the colour produced by various impurities. It forms the principal component of granite, porphyry, gneiss, etc. In the state of amorphous hydrates (SiO_2, nH_2O) it is found in various minerals, such as *agate*, *chalcedony*, *flint*, etc. As silicates it forms entire mountain ranges.

Amorphous silica is formed artificially by heating amorphous silicon in oxygen or air, or by heating silicic acid. It then forms a white amorphous powder of sp. gr. 2·2, which melts at very high temperatures in the oxyhydrogen flame and may be volatilised at the temperature of the electric arc.

It is insoluble in water and in all acids excepting hydrofluoric acid, which transforms it into silicon fluoride, SiF_4, and then into hydrofluosilicic acid. At high temperatures it is partially reduced by sodium and potassium to silicon, this reduction occurring more easily with magnesium and aluminium :

$$SiO_2 + Mg_2 = Si + 2MgO.$$

Whilst natural silica dissolves in hot solutions of sodium hydroxide when in a state of extremely fine division only, artificial silica dissolves much more readily. All varieties of silica are transformed into a glassy mass, soluble in water, called *soluble glass*, by fusion with the alkali hydroxides or carbonates; this substance consists of alkali silicates, Na_4SiO_4 and Na_2SiO_3.

Certain forms of apparatus are to-day made of quartz, for instance, crucibles, flasks, and thermometers in which the mercury is replaced by tin, etc., because they are very resistant to extremely high temperatures (up to 1600°) and to abrupt temperature changes. When such bodies are heated to redness they may be immersed immediately in water or even in liquid air without breaking, owing to the very small coefficient of dilatation of the quartz. In preparing such apparatus the quartz is melted in iridium vessels heated with a strong oxyhydrogen or oxyacetylene flame to 1850°–2000°. Such apparatus costs as much as platinum apparatus. (The price has recently been much reduced.—*Translator's note.*)

More economical forms of quartz apparatus are obtained by heating the powdered quartz until it becomes soft and the particles adhere to one another. The articles thus formed are not transparent and are glazed on the surface with the oxyacetylene flame.

Much quartz is used in the manufacture of glass, porcelain, sodium silicate, etc. For such uses the price varies from 14*s.* to £1 4*s.* per ton.

The cheaper quartz articles for laboratories cost four or five times more than similar articles of the best porcelain. It is found that during its use, for instance, for large vessels for the concentration of acids, very fine cracks are formed which slowly allow the acid to escape. This industry is still in its youth and further improvements will certainly take place.

SILICON MONOXIDE : SiO. In 1907 H. N. Potter reported that he had obtained this compound in the electric furnace according to the reaction, $SiO_2 + C = SiO + CO$, or $2SiO_2 + SiC = 3SiO + CO$. Up to the present, however, it is not very easy to distinguish chemically and physically between SiO and SiO_2.

SILICIC ACID: H_4SiO_4 (ORTHOSILICIC ACID)

The soluble alkali silicates when treated with hydrochloric acid yield a gelatinous mass of orthosilicic acid of the same character as that obtained from silicon fluoride and water:

$$Na_4SiO_4 + 4HCl = 4NaCl + Si(OH)_4.$$

This normal silicic acid, when washed and dried in the air, loses one molecule of water and is transformed into amorphous *metasilicic* acid, SiO_3H_2, which when heated to redness loses a further molecule of water, leaving silicon dioxide, SiO_2.

Since gelatinous silicic acid is slightly soluble in water, in dilute hydrochloric acid, and in soda, if a little sodium silicate is poured into dilute hydrochloric acid, gelatinous silicic acid is not separated but remains in solution together with the NaCl formed and with the excess of HCl. In order to separate the aqueous solution of NaCl and HCl from the silicic acid, a dialyser is employed, using the osmotic phenomenon studied by Graham (*see* p. 106).

Numerous *polysilicic acids* are known, in the form of salts or as natural silicates, and they may be supposed to be formed by the condensation of two or more molecules of silicic acid with simultaneous loss of one or more molecules of water. All these acids may be derived from the general formula, $m\mathrm{Si(OH)}_4 - n\mathrm{H_2O}$, where m indicates the number of molecules of orthosilicic acid which condense with separation of n molecules of water.

It is these polysilicates or polysilicic acids which actually exist in opal, agate, chalcedony, amethyst, etc.; when heated to redness these substances lose 5 to 15 per cent. of water.

The more widely diffused corresponding higher acids are: $H_2Si_2O_5$, $H_4Si_3O_8$, H_2Si_3O, $H_4Si_4O_{10}$, etc.

SILICON DISULPHIDE: SiS_2. This compound is obtained in an analogous manner to CS_2, *i. e.*, by passing sulphur vapour over hot amorphous silicon or by passing carbon disulphide vapour over a red-hot mixture of SiO_2 and carbon.

It is a solid substance which sublimes in the form of white silky needles, and is decomposed by water into silicic acid and H_2S.

A **SILICON NITRIDE**, Si_2N_3, is also known and is formed by passing dry nitrogen over red-hot amorphous silicon.

TITANIUM: Ti, 48.1; ZIRCONIUM: Zr, 90.6; THORIUM: Th, 232.42

These three elements belong to the group of the rare elements; they have the same analogy to the group of carbon and silicon as vanadium, columbium, and tantalum have to the elements of the phosphorus group.

They are also analogous to tin; thus they form basic compounds which are the more basic the higher their atomic weight. These compounds react with acids, forming fairly stable salts. They are tetravalent elements, and form compounds of the type, MX_4, whilst none of the type MX_2 are known, though such have been studied in the case of tin.

In the group of the rare earths, Urbain in 1909 was able to detect the presence of at least 16 rare elements (samarium, europium, gadolinium, neodymium, praseodymium, terbium, dysprosium, holmium, etc.).

TITANIUM: Ti, 48.1

This is a rather rare element which is found in certain minerals such as *rutile* (with about 50 per cent. TiO_2), *anatase* and *brookite*, which contain titanium dioxide, TiO_2;

perowskite contains calcium titanate, and ferrous titanate, $FeTiO_3$, and the silicotitanate constituting sphene or titanite, are also known.

Titanium was first obtained in the free state by Berzelius. It was recognised and studied as an element by Wöhler, who obtained it by heating potassium fluotitanate, TiF_6K_2, with potassium. It is to-day obtained from its oxide by heating it with finely divided aluminium. In 1910 Hunter obtained it in the pure state by heating titanous chloride with sodium to redness in a closed vessel. It forms a grey metallic powder or a metallic mass similar to steel, which is fairly hard and melts with difficulty, but may be worked at a red heat. It decomposes boiling water and dissolves in HCl or H_2SO_4 with evolution of hydrogen in the same manner as metals. It has the specific gravity 4·50 and melts between 1795° and 1800°. It burns when heated in the air. On account of its affinity for oxygen and nitrogen on heating, it is used by being added to steel in proportions up to 10 to 15 per cent., by which means the metal becomes much tougher than ordinary steel. Besides ferro-titanium, titanio-tungsten is also made for electric lamp filaments.

In 1911 the Central New York Railway had made 41,500 tons of ferro-titanium rails, containing 1 per cent. of an alloy with 10 per cent. of titanium.

Certain titanium compounds are used in the dyeing of cotton with basic dyes and on tannin mordant, and to give a yellow colour to porcelain.

Crude titanium costs £4 and the pure metal £8 per kilo. Ferro-titanium containing 20 per cent. of Ti costs 4*s*. to 6*s*. per kilo, and pure anhydrous titanic acid 28*s*. per kilo.

TITANIC CHLORIDE : $TiCl_4$. This is formed in the same manner as $SiCl_4$, by heating a mixture of titanium dioxide and carbon to redness in a current of chlorine.

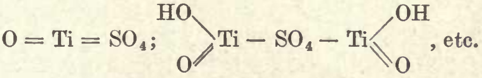
It is a colourless liquid which boils at 136° and fumes in the air forming HCl and titanic acid. Its specific gravity is 1·76. It decomposes with water into metatitanic acid (H_2TiO_3) and HCl.

Ti_2Cl_4 and Ti_2Cl_6 are also known, and so are hydrofluotitanic acid, H_2TiF_6, and the corresponding salts.

TITANIUM DIOXIDE : TiO_2. This compound is obtained by heating the acid or hydroxide to redness. It is a white amorphous powder, yellowish in the hot and is found crystalline in nature as *rutile*, *brookite*, and *anatase*. It is soluble only in boiling sulphuric acid and in HF, with which it forms the fluoride. When fused with alkalis it forms titanates, and on heating with gaseous ammonia it forms titanium nitride, TiN_2, which is a powder of an intense violet colour. **Titanium cyanonitride, Ti_5CN_4,** is also known, being formed in the slag of blast furnaces in which titaniferous iron ore is worked. It is there found in the form of cubes with a coppery-red metallic lustre.

TITANIUM PEROXIDE : TiO_3. This is obtained from solutions of titanic acid with hydrogen peroxide (*see* p. 267).

TITANIC ACID : H_4TiO_4. This compound is obtained in the free state by treating hydrochloric acid solutions of the titanates with ammonia. When dried over sulphuric acid it loses 1 mol. of water forming *titanium hydroxide*, TiO_3H_2, which may be considered as a *metatitanic acid*, because it forms salts with energetic bases (K_2TiO_3; $FeTiO_3$, etc.). Polyacids are also known. These compounds of titanium may also be considered as hydroxides, $Ti(OH)_4$ and $TiO(OH)_2$, because they have basic properties, and therefore also form salts with acids. Thus various sulphates are known, for example :



When titanium dioxide has been subjected to prolonged fusion with potassium bisulphate, it may be dissolved in cold acidified water, but titanic acid is precipitated on boiling. Addition of ammonia to the acid solution of a titanate causes precipitation of voluminous white hydrated titanic acid, $Ti(OH)_4$, which is only slightly soluble in alkalis but dissolves in acids and then gives with hydrogen peroxide an orange-yellow coloration which is not removed by ether, but is caused to disappear by stannous chloride and zinc dust.

ZIRCONIUM : Zr, 90.6

This element is rare, and is found in the form of silicate, $ZrSiO_4$ (*zircon*). It is obtained in the free state by a process analogous to that for obtaining titanium, and forms a black powder which burns easily; two other allotropic forms are also known, one crystalline and the other graphitic.

The *tetrachloride* and *tetrafluoride of zirconium* are known, $ZrCl_4$ and ZrF_4, and also *zirconium hydroxide*, $Zr(OH)_4$, which is obtained by precipitating a solution of one of its salts in a strong acid with NH_3, and forms a voluminous mass, insoluble in alkaline solutions. When, however, it is fused with alkalis, *sodium metazirconate*, Na_2ZrO_3, and *sodium zirconate*, Na_4ZrO_4, easily decomposable by water, are formed. The basic character of the hydroxide is shown by the salt which is obtained with sulphuric acid, $Zr(SO_4)_2$. When heated to redness, the hydroxide forms *zirconium dioxide*, which is also found crystallised in nature, and dissolves only in hot strong sulphuric acid, forming the above-mentioned sulphate; on fusion with alkalis it forms alkali zirconates and metazirconates, mentioned above.

When the oxide is heated to redness it emits a very intense white light which was used for preparing the first incandescent mantles for illumination. It is now also used for electric lamps.

Since the oxide melts at a very high temperature, it is used in the construction of crucibles which withstand even 2400°. It is used for special enamels and glasses resistant to boiling water and acids.

THORIUM : Th, 232.42

Until a few years ago very little of this element had been found; to-day, however, considerable quantities of its derivatives are produced for the preparation of the Auer incandescent mantles.

It was first extracted from *thorite*, $SiO_4Th, 2H_2O$, which is somewhat rare, although it contains 52 per cent. of thorium. To-day it is obtained from the more abundant *monazite*. In 1906 a very important monazite deposit containing up to 13·5 per cent. of thorium oxide was discovered in the Transvaal, and another large deposit was found in Brazil. In the United States of America 650 tons of monazite sand were produced in 1905, valued at £32,000, but in 1908 the production had already fallen to 200 tons, whilst 300 tons of thorium nitrate were imported. Crude monazite sand contains about 25 per cent. of true monazite and from 1000 tons, about 270 tons are separated (at the Centerville Mining Co., U.S.A.) by means of the electro-magnetic separator. Free *thorium* is obtained by heating the double chloride or double fluoride of thorium and potassium with metallic potassium or sodium. It forms a powder of metallic lustre of sp. gr. 11. It keeps well in the air up to temperatures of 100° to 120°, but on heating to higher temperatures it burns with a bright light producing the dioxide, ThO_2, also called *thoria*.

The oxide, and also the hydroxide, $Th(OH)_4$, possess no acid characteristics, as they do not dissolve or form salts with the alkalis, whilst ThO_2 dissolves only in concentrated acids such as HCl, H_2SO_4, and HNO_3 (but not in dilute acids), forming, for example, thorium sulphate, $(SO_4)_2Th, 9H_2O$, which is soluble in cold, but insoluble in hot water. Both the oxide and the sulphate are isomorphous with the oxide and sulphate of uranium. With regard to the radio-activity of thorium minerals, *see* p. 126.

THORIUM NITRATE is the salt most largely employed in the manufacture of Auer incandescent mantles and has the formula $Th(NO_3)_4 + 6H_2O$ when crystallised from hot solutions, but it sometimes contains only $5H_2O$, whilst from cold solutions it separates with $12H_2O$; these crystals lose $8H_2O$ at 100° and a nitrate containing $4H_2O$ (47 to 49 per cent. of ThO_2) remains, which is that commonly placed on the market. The anhydrous nitrate contains 55 per cent. of ThO_2, but it is not suitable as a commercial product, because on drying and heating it a portion may be decomposed. On heating to redness it is completely decomposed, forming the oxide ThO_2.

J. Koppel and H. Holtkamp (1910) prepared thorium nitrate from the hydroxide by pouring dry, finely ground monazite sand (containing, say, 5 per cent. of ThO_2 and 60 per cent. of rare earths) into twice its weight of hot, concentrated sulphuric acid in a cast-iron pan, the mass being heated until dense fumes are formed. The bulky, pasty sulphates (a lens should not reveal yellow grains of monazite sand) are poured into water, all the sulphates and the phosphoric acid passing into solution. After filtration, the thorium (together with a little cerium and didymium) is precipitated as phosphate by neutralising the solution with soda. The precipitate is filtered off, dissolved in concentrated hydrochloric acid and reprecipitated with oxalic acid. After several extractions with soda, the thorium oxalate passes into solution, while the impurities remain undissolved. From the solution the octahydrate is precipitated below 42° by sodium hydroxide (at a higher temperature the precipitate consists of the tetrahydrate, which filters badly), its complete purification being effected by redissolving it in HCl and precipitating with sulphuric acid; use is then made of the solubility of the sulphate in ice-water and of its gradual separation as hydrated sulphate when the temperature is suitably raised. By addition of ammonia this sulphate is reconverted into the hydroxide (if necessary, this process of purification is repeated several times), which is dissolved in nitric acid, evaporation of the solution then giving pure dry thorium nitrate.

T. Smith and C. James (1912) and O. Knöfler (Ger. Pat. 266,459, 1912) separate the thorium from all the other rare earths by means of the insoluble salt it forms with sebacic acid (*see* Vol. II. " Organic Chemistry "): 500 litres of the sulphuric acid solution obtained from the monazite sand (containing 8·5 kilos of ThO_2) are partly neutralised with about 16 kilos of magnesia, without precipitating the phosphates, and to the cold solution is added, with stirring, a solution of 7·6 kilos of sebacic acid in 300 litres of boiling water. The precipitate is filtered off in the hot and washed with hot water, and the almost pure thorium sebacate dissolved in sulphuric acid and the thorium precipitated by means of oxalic acid; the precipitated oxalate is washed with hot water to remove the sebacic acid (to be used again) and then heated, a yield of about 93 per cent. of ThO_2 being obtained. The thorium sebacate may also be decomposed with a hot 10 per cent. sodium carbonate solution, the products being sodium sebacate solution and insoluble thorium carbonate, which is converted into the nitrate by nitric acid; the yield of recovered sebacic acid is about 92 per cent. The thorium oxalate or carbonate may be purified further by the usual methods.

The pure nitrate costs about £1 12*s.* per kilo, the price being £100 in 1894, £26 in 1895, £6 8*s.* in 1896, and £2 in 1898. The world's consumption of thorium salts in 1910 was about 160 tons, 2000 tons of monazite with a mean content of 5 per cent. of ThO_2 being treated.

In 1913 *France* imported 21·2 tons of nitrates of thorium, cerium, etc., in 1914 20·6 tons, and in 1915 35·5 tons.

THORIUM CHLORIDE, $ThCl_4$. This compound is obtained from thorium and hydrogen chloride vapour or from the oxide or hydrate and concentrated hydrochloric acid. It melts at a white heat and then sublimes in white crystals. It is soluble in water from which crystals of $ThCl_4,8H_2O$ may be obtained. It forms double salts with other chlorides.

THORIUM HYDROXIDE, $Th(OH)_4$. This is obtained as a gelatinous precipitate by treating solutions of thorium salts with ammonia. When heated to redness it forms a mass of thorium dioxide, ThO_2. The hydroxide, $ThO(OH)_2$, is not known.

RARE EARTHS FOR INCANDESCENT LIGHTING

The first use of earths for this purpose was in the lime-light, in which a very vivid white light is obtained by heating a piece of calcium oxide in the oxy-hydrogen flame, but the quicklime soon crumbles, because it rapidly absorbs moisture and carbon dioxide from the air.

In 1880 Auer von Welsbach[1] utilised the property of thorium oxide of emitting an intense white light at a lower temperature than zircon in the ordinary Bunsen gas flame.

It was then found that pure thorium dioxide gives a less intense light than when it contains very small quantities (1 to 2 per cent.) of cerium oxide, which fact is probably explained by the catalytic action which this latter compound exercises during the combustion of the gas, which it accelerates greatly, since the temperature is higher than that obtained by ordinary combustion, and thus at this higher temperature the thorium oxide emits more light.

The raw material used for obtaining the rare earths is *monazite*, the discovery of which has saved the lighting gas industry from the competition of the electric light, and to-day

---

[1] Berzelius had already observed that when zircon is strongly heated much light is emitted. In 1868 Caron determined the luminous intensity of the light at the temperature of the oxy-hydrogen flame, and then Tessié du Motay at once attempted the first application of this light by employing the hydrogen flame in order to render zircon incandescent. In 1885 Linnemann prepared small discs of zircon and of zirconia adapted for incandescent burners, and W. Kocks discovered methods of giving any desired form to the oxide.

in many places illumination with incandescent gas mantles is more advantageous than with incandescent electric lamps, or in some cases even than the electric arc.

The monazite, which is composed largely of phosphates of cerium, didymium, and lanthanum, contains mixed with it various quantities of thorium minerals (3 to 10 per cent.). The composition of this mixture is: up to 28 per cent. of cerium oxide, 15 per cent. of didymium oxide, 13 per cent. of lanthanum oxide, 26 per cent. of phosphoric acid, 5·5 per cent. of alumina, 3 per cent. of titanic acid, and 6 per cent. of ThO_2.

The cerium and aluminium are separated by forming the corresponding basic sulphates, which are insoluble. Didymium and lanthanum remain together in solution and are transformed into double nitrates, that is, nitrates of the metal and ammonia. The separation of all these elements of the rare earths is somewhat complex, but is performed by utilising the properties possessed by their various salts (sulphates, nitrates, etc.) of being more or less soluble in the hot or in the cold, and by certain other salts (nitrates) of being more or less resistant to heat. The purity of the separate salts is then controlled spectroscopically, and that of the cerium by determining the amount necessary to add to thorium oxide to give a definite luminosity.

To obtain incandescent mantles for gas flames, Auer prepared a netted fabric of cotton or linen (now made of artificial silk) and formed a species of lengthened cone (mantle). He then soaked this in a concentrated solution of thorium nitrate containing 1 to 2 per cent. of cerium oxide, allowed it to dry and then burnt away the cotton fabric; the remaining skeleton, which has the same form as the fabric, is heated to redness in a strong Bunsen flame, using compressed gas. A maximum contraction and a certain consistency are thus obtained, which are further increased by immersing the mantle in an ether-alcoholic solution of collodion and then drying it in suitable chambers. These mantles are mounted on special burners of ordinary gas and then show the intense incandescence which we all know. Thorium oxide gives a bluish-white light; lanthanum oxide a pure white light; yttrium, yellowish-white; zircon, very white; cerium, reddish-white. By using different mixtures of these oxides the various lights may be modified or corrected.

Mantles made with cotton undergo deformation and contraction when ashed, so that they may be replaced with advantage by those made from ramie or artificial silk. For the saving of gas effected by the incandescent mantle, *see* Vol. II., " Organic Chemistry."

Pictet has prepared special mantles which may be used with gas mixed with oxygen and are capable of resisting temperatures up to about 3000°.

During the last few years Nernst has brought out a new electric incandescent lamp based on the observation that a filament formed of magnesium oxide mixed with a little zirconia, thoria, yttria, etc., does not conduct the electric current in the cold, but passes the current when gently heated, the filament then becoming incandescent.

The world's production of Auer and other similar mantles is stated to have been 220,000,000 in 1908, of which about 100,000,000 came from Germany, 55,000,000 from America, 35,000,000 from England and British Colonies, 15,000,000 from France, 3,000,000 from Austria, 2,500,000 from Italy, 2,000,000 from Belgium, and 1,500,000 from Russia.

In 1906 Germany exported Auer mantles to the value of £460,000. Smaller quantities are exported to-day, as large numbers of works have been erected in almost every country. Mantles of very poor quality at low prices are to-day placed on the market, but the price is always disproportionate to the value. In dealing with these products it would be advisable always to determine their illuminating value by means of photometric measurements.

BORON: B, 11

This is an element which it is difficult to connect with the other groups of elements. It has many resemblances to the metals, although it has decided non-metallic properties. Thus its oxy-compounds have an acid character. In nature it is found in a state of combination only, as boric acid, $B(OH)_3$; sodium tetraborate (*tinkal*), $Na_2B_4O_7 + 10H_2O$; *borocalcite*, B_4O_7Ca (of which a large deposit has recently been found in the Argentine); as *boracite*, $(2Mg_3B_8O_{15}) + MgCl_2$, at Stassfurt; as *larderellite*, $(NH_4)B_8O_{13}$, $4H_2O$, and as *colemanite*, $Ca_2B_6O_{11}$, $5H_2O$, in California; (*pandermite* and *priceite* are crystallographic varieties of colemanite). *Ulexite* or *tiza* is a sodium and calcium borate, $Ca_2B_6O_{11}$, $Na_2B_4O_7$, $16H_2O$.

Boron compounds are employed for various purposes, such as in medicine, in connection with soldering, in the preparation of fusible enamels, glass, earthenware, etc.

These minerals are abundant in volcanic territories, such as California, India, Chili, and the Argentine, and their origin is explained by the property possessed by many of these salts, which accumulate at the bottom of dried-up seas, of being easily carried through the strata of the terrestrial crust by means of steam. Sea water contains about 0·2 grm. of boron per cu. metre. Boron is widely diffused in small quantities throughout the earth and is thus found in the ash of many plants. It was discovered in 1807 simultaneously by Davy in England and by Gay-Lussac and Thénard in France.

Free boron is obtained by reducing boric acid or borax with K, Na, Mg, Al, or P in the hot. Moissan has recently obtained it in the electric furnace. It forms masses of a red or yellow colour, but sometimes colourless, which dissolve in molten aluminium and gradually separate "*crystalline boron*" on cooling; this was obtained long ago by Wöhler and by St. Claire Deville, and resembles diamond in its refractive power, hardness, brilliance, and resistance to heat and chemical reagents. Its specific gravity is 2·68. "Crystalline boron" is more stable than amorphous boron and volatilises only at the temperature of the electric furnace. In 1909 Binet de Jassoneix showed that "crystalline boron" is really aluminium boride, AlB_2, which sometimes forms mixed crystals with aluminium carbide, Al_4C_3. Amorphous boron forms a brown powder which when finely powdered easily absorbs gases and has a marked catalytic influence on various reactions. It burns at 300° with a green light, forming B_2O_3 and BN (boron nitride). Crystalline boron is not attacked by acids or by dissolved alkalis, and is dissolved only when fused with solid alkali hydroxides or carbonates. When it is heated to redness in presence of steam or of H_2S hydrogen is evolved. It has a very low specific heat and, therefore, a very low atomic heat, which increases at high temperatures (*see* p. 113), indicating that at low temperatures boron has a very large complex molecule.

Graphitic boron costs up to £400 per kilo, crystallised boron £260, and amorphous boron £32.

BORON HYDRIDE : BH_3. This compound is a gas and is obtained mixed with hydrogen by heating magnesium with boron trioxide, and then treating the resulting mass with HCl; the gas, which contains BH_3 and H, is only slightly soluble in water, burns with a green flame and is decomposed by $AgNO_3$. At a red heat it is dissociated into H_3 and B, and in a red-hot glass tube deposits of boron are formed.

The hydrides, B_2H_6, B_4H_{10} and $B_{10}H_{14}$ are also known. When B_4H_{10} is heated to 100°, three solid boron hydrides are obtained, one ($B_{10}H_{14}$) volatile in a vacuum and two non-volatile, viz., one colourless and soluble in CS_2 and the other yellow and insoluble; at 150° the colourless variety yields hydrogen and the yellow modification (A. Stock, 1913).

BORON TRIOXIDE, BORIC ANHYDRIDE : B_2O_3. This compound is formed on burning amorphous boron in oxygen, and is prepared practically by heating boric acid to redness:

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$

It forms a hard, amorphous, glassy mass which volatilises only at a white heat, and on heating displaces even the more energetic acids from different salts and dissolves many metallic oxides, forming a kind of glass, which is often coloured (*borax beads*, by which various metals may be recognised in chemical analysis). In the air it is slowly transformed into boric acid.

BORIC ACID : BO_3H_3 (BORACIC ACID)

In the Tuscan marshes and especially at Lardarello and the vicinity, *soffioni* (also called *fumaroles*) of very hot steam escape from certain crevices in the ground. These contain a small quantity of boric acid together with CO_2, NH_3, SH_2, and a little ammonium sulphate. On condensing these vapours in vats of water called *lagoni*, and concentrating the dilute (2 per cent.) solution, crystalline boric acid separates. During the last few years, thanks to the work of Professor Nasini, the utilisation and treatment of these *soffioni* have been rendered more rational and the heat of the gases has also been employed and the boric acid completely refined.[1] Crystallised boric acid is also found in the earth in Tuscany under the local name of *sassolino.* It is abundant in Thibet and California in the form of sodium borate (tinkal).

Considerable quantities of boric acid are nowadays prepared—and compete with that obtained from Tuscany—by decomposing the boracite which is abundant in the upper layers of the Stassfurt salts (*Abraumsalze*). The powdered boracite is mixed to a paste with a little dilute HCl and then poured into boiling water. The clear solution is decanted off, saturated, and while still hot is poured into lead-lined vessels where the boric acid crystallises on cooling. It is then recrystallised from boiling water in stone vessels which are slowly cooled. In the laboratory the whole of the boric acid may be extracted from mother-liquors or other impure products by shaking the liquid with ether or with chloroform, which dissolves all the boric acid and does not mix with the water; on decanting the new solution and evaporating the solvent, which may be recovered in a condenser, pure boric acid remains.

Th. Heidlberg proposed the following economical process in 1907: 500 kilos of finely ground borocalcite are poured with efficient stirring into a boiling solution of sodium bisulphate of 15° Bé. containing 850 kilos of crude bisulphate; after an hour the whole is passed through a filter-press and the calcium sulphate which is retained is washed with hot water. The whole of the liquors are then concentrated to 30° Bé., after which 430 kilos of crude boric acid separate on cooling and are converted into the commercial quality by one recrystallisation. The mother-liquors after further concentration deposit very fine crystals of sodium sulphate; the last mother-liquors are used for treating new portions of boracite.

The minerals contain from 5 to 35 per cent. of B_2O_3 and 2 to 4 tons of crude borax are needed for the preparation of 1 ton of boric acid.

Pure boric acid is obtained by mixing a saturated boiling solution of sodium borate with HCl or H_2SO_4; on cooling, crystals of boric acid are obtained, which are purified by recrystallisation from water. It is obtained in large, light, shining scales if a small definite amount of an albuminous substance is added to the solution. In the cold it dissolves in water to the extent of 4 per cent., and on heating, up to 33 per cent.

The solution turns blue litmus paper feebly red and yellow turmeric paper brown in common with bases which, however, do not redden litmus; very small quantities of boric acid may be detected with turmeric.

L. Robin (1913) detected as little as 0·000027 mgrm. of boric acid by adding alcoholic extract of mimosa flowers and 1 to 2 drops of dilute sodium hydroxide solution, decolorising the yellow solution with 2 to 3 drops of dilute HCl, evaporating to dryness and moistening the residue with concentrated ammonia solution: a red or blood-red coloration is thus obtained.

When dissolved in alcohol (better, methyl alcohol), even in small amount, it burns with a green flame and it may be distilled in considerable quantities

---

[1] At Lardarello the boraciferous *soffioni* have a pressure of 2 to 3 atmos. and a temperature of 150° to 190° and serve to concentrate the boric acid solution. In 1903 attempts were made to utilise the steam from the *soffioni* directly in steam engines, but owing to the corrosion produced by the salts, H_2S, etc., it is better to use it to heat multi-tubular boilers fitted with aluminium tubes. In this way a 9000-kilowatt generating station is operated, the power being obtained from three turbo-alternators and the electrical energy transmitted to Florence, Leghorn, etc.

According to Porlezza and Norzi (1913), the percentage composition of the gas from the *soffioni*, after the boric acid, water vapour, etc., have been condensed, is: CO_2, 92·20; H_2S, 2·0; CH_4, 1·78; H, 2·45; O, 0·18; N, 1·35; Ar, 0·0245; He, 0·0155.

in a current of steam. Boric acid is used in large quantities in medicine, especially by oculists, as a useful though mild antiseptic. Its use is greatly abused as a preservative for foodstuffs, such as vegetables, tomatoes, etc. On heating for a long time to 80° to 100° it loses one molecule of water and forms metaboric acid.

STATISTICS AND PRICES. The production and price of boric products in different countries are very variable and are shown in the footnote.[1]

METABORIC ACID : $BO \cdot OH$, is vitreous and is obtained from boric acid (*see above*). It melts at 160°, being transformed into

TETRABORIC ACID : $H_2B_4O_7$, according to the following equation :

$$4BO_2H = H_2O + H_2B_4O_7.$$

[1] World's output of natural boric compounds. The numbers represent tons:

	U.S. (borates)	Chili (calcium borate)	Italy (crude boric acid)	Peru (calcium borate)	Argentine (calcium borate)	Turkey (calcium borate)
1900 . . .	26,387	13,177	2491	7080	—	—
1903 . . .	31,235	16,879	2583	2466	—	—
1906 . . .	52,774	28,996	2561	2451	—	—
1909 . . .	37,589	32,218	2431	2870	805	14,000
1911 . . .	—	—	2648	—	—	—
1912 . . .	—	—	2309	—	—	—
1914 . . .	—	—	2537	—	—	—
1915 . . .	—	—	2497	—	—	—
1916 . . .	—	—	2293	—	—	—

In 1912 Germany imported almost 16,000 tons of borates, worth about £160,000, about 10,000 tons from Chili and 3000 from Peru; the imports included also about 8000 tons of boric acid in 1912, 3300 tons of the refined acid, valued at £80,000, being exported.

California in 1911 produced 53,000 tons of borocalcite.

England imported 20,000 tons of borocalcite (£176,000) in 1911.

France imported 74·3 tons of boric acid in 1913, 66·6 in 1914 and 78·6 in 1915, and exported 2994 tons in 1913, 2089 tons in 1914, and 1434 tons in 1915.

In the United States the output of pure boric acid was 1200 tons in 1900, 3100 tons in 1905, and 2775 tons (£58,000) in 1910.

Before the European War, Turkey consumed more than 150 tons of boric acid per annum.

In Italy the output of refined boric acid was 87 tons in 1893, 166 in 1898, 284 in 1900, 239 in 1902, 749 in 1905, 466 in 1907, 444 in 1911, 838 (£19,455) in 1914, and 1277 tons (£43,410) in 1915.

The Italian imports and exports of boric acid are as follows :

	Imports	Exports	
	Refined acid	Crude acid	Refined Acid
	Tons	Tons	Tons
1894–1898 (mean)	56·4	1740	—
1899–1903	31	1730	119
1904	39·2	738·4	220
1905	—	1645	268
1906	14·6	1675	494
1907	49·6	857·6	384
1908	74·6	636	339
1909	66	837	686
1910	87	893	547
1911	113 (£2660)	903 (£15,185)	381 (£8840)
1912	74	849	725
1913	21	771	571
1914	3 (£92)	669 (16,065)	521 (£16,672)
1915	0·2	367	1185
1916	1·4	274 (7680)	1293 (£49,138)

The price of refined boric acid forty years ago was £260 per ton and in 1913 about £28 (£26 for powder, £30 for large scales). Crude boric acid costs £14 to £16 per ton.

This in turn loses the final molecule of water at a red heat, forming two molecules of boric anhydride, B_2O_3.

The more important salts are formed from tetraboric acid, and **Borax**, which is the commonest of all, is a sodium tetraborate, $B_4O_7Na_2$ (*see* Part III).

HALOGEN DERIVATIVES OF BORON

BORON CHLORIDE : BCl_3, is obtained by heating boron in a current of chlorine, or a red-hot mixture of B_2O_3 and carbon in presence of chlorine. It is a liquid which boils at 18°, has a specific gravity of 1·25, and is decomposed by water :

$$BCl_3 + 3H_2O = BO_3H_3 + 3HCl.$$

The *bromide, iodide,* and *fluoride* of boron are also known.

The last-named is a gas which is very soluble in water, and is obtained in an analogous manner to silicon fluoride. With HF it forms *hydrofluoboric acid,* BF_4H, a very energetic monobasic acid, more especially known in its salts, which are not very soluble.

BORON NITRIDE : BN. Amorphous boron is one of the few elements which combine directly with nitrogen when heated to redness, with formation of a nitride. With NH_3 boron also forms BN, and develops H. Boron also burns with a bright light in an atmosphere of nitrous oxide, forming B_2O_3 and BN.

BN is prepared in practice by heating 1 part of boric anhydride to redness in a platinum crucible with 2 parts by weight of ammonium chloride or with urea, and washing the residue with HCl.

Stähler and Elbert (1913) prepared the nitride by heating a mixture of B_2O_3 and charcoal in nitrogen at 1500° to 1700°; at the ordinary pressure the yield is 28 per cent., but this is increased to 85 per cent. at high pressures. It is more convenient to heat a mixture of borocalcite and carbon in nitrogen for 30 minutes at 1850° or for 15 minutes at 1400°; in this case the pressure is without influence : $CaB_4O_7 + 8C + 3N_2 = 4BN + CaCN_2 + 7CO$.

It forms a white amorphous powder which is not altered even when heated to redness in the air. It is insoluble in water, in acids, and in dilute alkalis. It is decomposed by steam at 200° : $BN + 2H_2O = BO_2H + NH_3$. It combines with HF, forming ammonium borofluoride : $BN + 4HF = BF_4NH_4$. On heating over the blowpipe BN forms B_2O_3. In presence of graphite and nitrogen it is stable even at 2400°.

BORON SULPHIDE : B_2S_3, is also known, and is obtained by burning boron in sulphur vapour, or by heating amorphous boron to redness in a current of H_2S; also from a mixture of B_2O_3, carbon and carbon disulphide vapours. It forms white silky crystals, which are violently decomposed by water : $B_2S_3 + 6H_2O = 3H_2S + 2B(OH)_3$.

BORON CARBIDE : B_2C_2, is known, but more closely investigated is the carbide B_6C, which is prepared in the electric furnace from boron and carbon in presence of copper. The copper is then removed from the fused mass by the action of HNO_3, and black shining crystals of extraordinary hardness, greater than that of carborundum, remain.

A BORON PHOSPHIDE : BP, also exists.

PART III. METALS

The distinction of this numerous group of elements, the metals, from those which we have already studied as non-metals, is not very rigorous, and although for some elements many of the physical and chemical properties differ very greatly, other properties are common; various members of the one group or the other possess both metallic and non-metallic properties, so that they cannot strictly be considered to belong to the one group much more than to the other.

The more or less metallic external appearance and conductivity for electricity and heat are differential characteristics only in a relatively quantitative sense, and the same may be said of the fact that oxygen compounds of the non-metals ordinarily form acid substances, whilst the oxygenated compounds of the metals in general are basic substances, for here also the exceptions are numerous. The valency of the metals with respect to oxygen diminishes with rise of the temperature, and in general the compounds containing the minimum of oxygen are the more stable at higher temperatures, whilst at ordinary temperatures those containing the maximum of oxygen are more stable.

The metals do not form gaseous hydrogen compounds, and give chlorides which are stable in contact with water. When any substance which contains both a metal and a non-metal is decomposed by electrolysis, the metal is always formed at the negative pole, whilst the non-metal separates at the positive pole. Excepting mercury the metals are all solid and have a specific gravity which varies from 0·59 to 22·5 (*see* Table on p. 514) and ordinarily increases with increase of the atomic weight. This relation becomes more evident if the atomic volumes of the metals are compared, that is, the ratios between the atomic weight, A, and the specific gravity, d: atomic volume $= \frac{A}{d}$. Those metals which have a specific gravity lower than 5 are called the *light* metals and the others the *heavy* metals.

Almost all the metals are more or less ductile and malleable.

The *malleability* of metals, that is, the property of being convertible into very thin sheets by hammering, and the *ductility*, that is, the capacity for being drawn into very thin wires, vary with the temperature. For iron they attain a maximum at a red heat, whilst zinc is malleable between 100° and 150° and becomes brittle at 205°. In the scales of ductility and malleability all metals do not follow the same order, so that two metals which are very close together in the scale of malleability may be somewhat far apart in the scale of ductility and *vice versa*. With suitable precautions, gold leaf has been obtained of a thickness of only 0·0001 mm. and platinum wires of a diameter of 0·00008 mm.; gold and silver leaf of these very small orders of thickness are almost transparent between 200° and 500°.

When molten metals are cooled in a suitable manner crystals of the regular or hexagonal rhombohedric systems are sometimes obtained.

Metals may also occur in allotropic forms, crystalline or amorphous. In certain cases the same metal may possess various specific gravities according as it has been rolled, hammered, or molten, and may acquire different degrees of brittleness at various temperatures; also the heat of oxidation is not always the same. Allotropy also includes the passive form of certain metals. In the allotropic passive form under certain conditions the metals resist the action of acids and behave electrolytically in a different manner from the active form.

The hardness and brittleness of metals are extraordinarily modified by minimal traces of impurities. Thus gold becomes extremely brittle when it contains $\frac{1}{2000}$ of lead; iron containing minimal quantities of carbon becomes very hard (steel), and acquires well-marked special properties with traces of vanadium, Mn, etc.; lead containing 3 parts per 1000 of antimony becomes very readily oxidisable when liquefied, so that it even catches fire. We shall see later, on studying alloys, what a great influence even small quantities of a given component may have in modifying not only physical properties, but also the chemical properties of the alloy.

Kahlbaum in 1902 and Moissan in 1906 succeeded in distilling numerous metals in porcelain tubes with the oxy-hydrogen flame in an almost absolute vacuum (down to two-millionths of a millimetre). Kahlbaum thus obtained about 25 metals in an extremely pure condition, often crystallised in an allotropic form. It has been sometimes observed that certain easily fusible metals volatilise with difficulty (tin); osmium volatilises without melting, whilst in general of two metals that which boils first also melts first. Certain metals, such as copper and silver, absorb oxygen during fusion and liberate it again at the moment of solidification (*recalescence*). Palladium is capable of absorbing 936 vols. of hydrogen.

The metals are more porous when hot, and gases then pass through their pores with greater facility.

The *specific heat* of metals is influenced by the temperature, and in general is diminished by lowering the temperature, the diminution being greater the smaller the atomic weight (*see* p. 112).[1]

It has now been shown that the molecules of the metals are monatomic. This result is obtained from their vapour densities, from the diminution of the vapour pressure of mercury in which they are dissolved, and from the freezing-point of the metallic alloys, which are true solutions of metals.

Metals may thus be considered as elements the molecules of which are formed of a single atom, and this explains both the great reactivity of most of them and also their electrical conductivity.

Metals act as cations and conduct the electric current without simultaneous transference of matter and without alteration. They are, therefore, called conductors of the first class in distinction from electrolytic conductors (solutions) which are conductors of the second class and decompose, matter being transported during conduction. The electrical conductivity of metals increases with diminution of the temperature, and it appears that in the vicinity of absolute zero their conductivity is very great, whilst on the other hand the conductivity of electrolytes (solutions) diminishes with fall of the temperature.

Endeavours have recently been made to explain the electrical conductivity of metals by the hypothesis that in the metals themselves there are very numerous non-material electric particles, similar to ions, which impart to them

---

[1] The heats of fusion (*f*) and the calorific capacities of the fused metals (*c*) in Cals. are as follows: Na: f 32, c 78; Mg: f 58, c 246; Al: f 100, c 258; Si: f 128, c 555; K: f 16, c 27; Ca: f 53, c 186; Fe: f 69, c 336; Ni: f 68, c 290; Co: f 68, c 329; Cu: f 43, c 162; Zn: f 23, c 68; Ag: f 24, c 89; Cd: f 13, c 32; Sn: f 14, c 28; Sb: f 40, c 74; Ir: f 28, c 113; Pt: f 24, c 89; Au: f 16, c 51; Pb, f 4, c 16; Bi: f 12, c 21; a solder containing 50 parts of Sn and 50 of Pb has f 10 and c 19. For bronze and brass c is about 120, for cast-iron about 230 and for steel about 290. Thus, the heat necessary to bring steel to the melting-point and that necessary for complete fusion at that temperature are together about 290 Cals. (Richards and Neumann, 1912).

the property of conducting the current. The metals may then almost be considered as solutions of electric particles.

The magnetic elements, which are attracted by the magnet, are the following, arranged in decreasing order: Fe, Ni, Co, Mn, Cr, Ce, Ti, Pd, Pt, Os.

The non-magnetic metals, which are not attracted by a magnet, may be arranged in the following order, commencing with those which are least magnetic: Bi, Sb, Zn, Cd, Na, Hg, Pb, Ag, Cu, Au, As, U, Rh, Ir, W; naturally the final terms of the two series approach one another in properties, so that uranium and iridium are sometimes classed amongst the magnetic metals. Certain metallic compounds, such as oxides and peroxides, are also magnetic. The magnetism of iron disappears at 740°, that of nickel at 340°, and that of cobalt at 900°. The spectroscopic behaviour of metals has already been discussed at length in Part I (p. 55).

During the past few years the system of metallisation in the cold by means of direct powdering of fused metals on to the most varied surfaces (wood, glass, paper, metals, fabrics, etc.) has attained some practical importance. The process was rendered practicable by Schoop, who first projected very finely powdered metal through the flame of a blowpipe by means of compressed air. He then replaced the air by an inert gas (N, CO_2, etc.), and the powdered metal by a metallic wire which, by suitable gearing (worked by the compressed gas itself), is introduced regularly and continuously into the oxy-hydrogen flame while an air jet pulverises it and projects it against the object to be coated, at a distance of 15 to 20 cm. from the flame. The imponderable drops solidify immediately they leave the flame, and on impinging on the surface of the object are heated to fusion and adhere stably to one another and to the cold object. The wires used are 0·4 to 0·7 mm. thick with hard metals (copper, bronze, brass, aluminium, etc.), and 2 to 3 mm. thick with soft metals (lead, zinc, etc.). Metal objects should first be well cleaned by scraping or sand-blasting, since otherwise the drops do not adhere well. This process is used not only to coat iron with lead (replacing the slow and costly autogenous lead-coating), copper, etc., but also for taking impressions of models, etc., since, if the object is first smeared with dust or a liquid, the metallic pellicle will be detachable with faithful reproduction of all the detail. Beautiful metallic decorations may be produced on textiles and on articles of clay, glass, wood (cornices, etc.), etc.

The table on page 514 gives the more important physical data relating to the metals.

METALLIC ALLOYS

All the metals more or less easily form alloys, which cannot be considered as simple mechanical mixtures, as the union is more intimate and occurs between molecule and molecule through the agency of fusion, it being then no longer possible to separate the components mechanically. Alloys may be compared rather with solutions, and may thus be considered as true solid solutions, and when they are melted consist of nothing but liquid metallic solutions.

On the other hand, the alloys are not homogeneous chemical combinations, that is, the components are mixed not merely in the ratio of their atomic weights, but also in the most varied proportions, and just as in ordinary solutions of salts the solubility varies with the nature of the solvent and of the dissolved substance, so also is this the case for two or more molten metals. These sometimes mix in any proportion whatever, but in certain cases only in well-defined proportions.

The rules which regulate solutions, chemical equilibria and the phase rule may also be applied, with proper precautions, to molten alloys.

The eutectic temperature of alloys corresponds with the cryohydric temperature of ordinary solutions (pp. 122 and 257).

PHYSICAL CONSTANTS OF METALS

Metal	Melting-point	Boiling-point approx.	Hardness Pb = 1	Density Water = 1	Specific heat	Linear coefficient of expansion between 0° & 100° per 10,000,000	Electrical conductivity Ag = 100	Thermal conductivity Ag = 100
Aluminium	645°	1800°	17·3	2·56	0·2143	234		
Antimony	632°	1440°		6·72	0·0523	116	4·62	
Arsenic	500°			5·67	0·0830	60	4·76	
Barium	850°			3·75				
Bismuth	267°	1420°	3·3	9·82	0·0308			
Cadmium	321°		6·9	8·65	0·0567	137	1·25	
Caesium	26·4°			1·88		310	32·72	1·8
Calcium	780°		1·9 (?)	1·83	0·1722			
Cerium	645° (?)			6·63	0·0448			
Chromium	1520°			6·8	0·1216			
Cobalt	1478°			8·5	0·1067			
Columbium				6·27		124		
Copper	1085°	2310°	19·3	8·93	0·0952			
Gallium, solid	30°			5·96	0·079	70	99·95	73·0
Germanium	900°			5·47				
Glucinum	1800°			1·64	0·4084			
Gold	1054°		10·7	19·3	0·0324	145	77·96	53·2
Indium	154·5°			7·42	0·0574	459	18·61	
Iridium	2300°			22·42	0·0326	70		
Iron	1530°	2450°		7·8	0·1138	123		11·9
Lanthanum				6·19	0·0448			8·5
Lead	327°	1525°	1	11·38	0·0315	280	8·32	
Lithium	186°			0·59	0·9408			
Magnesium	750°	1120°		1·74	0·2499	276		
Manganese	1260°	1900°		8·0	0·1217			
Mercury	−38·4°			14·4	0·0319		1·61 (liq.)	
Molybdenum	2500° (?)			8·6	0·0722			
Nickel	1452°			8·8	0·1092	129		
Osmium	2700° (?)			22·48	0·0311	66		
Palladium	1550°			11·5	0·0593	119		
Platinum	1775°		24·0	21·5	0·0324	91		8·4
Potassium	58°			0·86	0·1655	842	22·62	
Rhodium	1920° (?)			12·1	0·0580	85		
Rubidium	38·5°			1·52				
Ruthenium	1950° (?)			12·26	0·0611	99		
Silver	962°	1955°	13·3	10·51	0·0570	194	100	100
Sodium	97·6°			0·97	0·2934	711	40·52	
Strontium				2·50				
Tellurium	451°			6·25	0·0525	173		
Thallium	302°			11·86	0·0336	302	9·16	
Thorium	above 1700°			11·1	0·0276			
Tin	232°	2270°	1·7	7·29	0·0562	227	12·36	14·5
Tungsten	3000°			19·13	0·0334			
Uranium	1500° (?)			18·69	0·0277			
Vanadium	1720°			5·5				
Zinc	419°		11·7	7·15	0·0956	291	29·02	19
Zirconium				4·15	0·0660			
Brass								23·1
White Metal								6·3

Guillemin, Sorby, Martens, Widmanstätten, and others have conducted micrographic analyses by attacking the surfaces of well-polished alloys with cold dilute nitric acid, or with dilute sulphuric acid (1/10) under the influence of a weak electric current (2 volts at $\frac{1}{10}$ of an ampère); they then examined the washed corroded surfaces under the microscope and photographed them, since in this way curious crystalline figures are rendered evident which are constant and characteristic for each alloy of definite compositions.

Microphotographs of alloys of bismuth, tin, and antimony are illustrated in Figs. 203 and 204, which we shall study later, and in these crystals of characteristic form are clearly shown. Other microphotographs are reproduced and explained in detail later in the chapter on Iron.

The microscopic study of alloys has greatly helped the elucidation of their internal constitution. In solidified alloys certain crystals of constant chemical composition different from that of the alloy may sometimes be isolated by suitable solvents and may be considered as true chemical combinations. From an alloy of 1 part of copper with 2 parts of tin, shining scales, unattacked by the acid, and of the formula, $SnCu_3$, may be obtained by treating it with concentrated cold HCl.

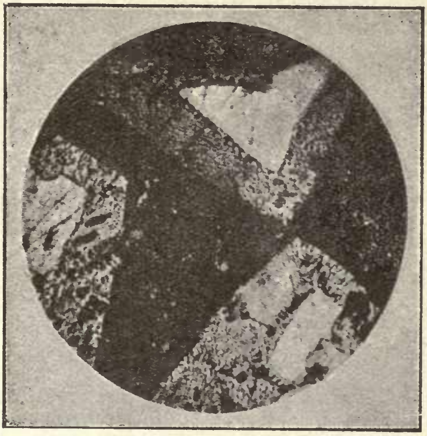


FIG. 203.

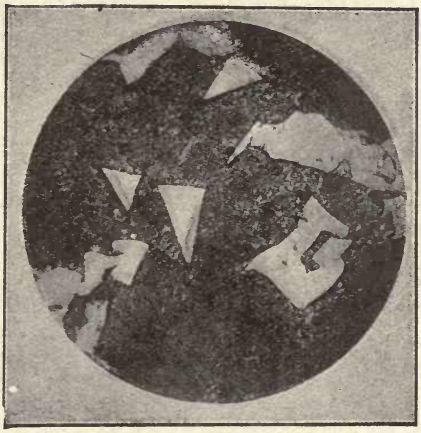


FIG. 204.

With metallic alloys the electrical conductivity is generally lower than the mean conductivity deduced from those of the component metals, because the alloy may be considered as a thermo-couple formed by its components, the electro-motive force of which acts in opposition to that producing the current. From the electrical conductivity of an alloy its composition may also be deduced, and one may decide whether the metals are present in combination or not by remembering that chemical combination tends to lower the conductivity. The compound $SnCu_3$ was detected in this particular manner.

By investigating the molecular weights of metals on the basis of the distribution law in solid and liquid solvents, Padoa and Bovini (1913) found that cadmium is monatomic in solution in tin, either in the solid or in the liquid phase.

Alloys generally melt at temperatures lower than their components; thus on mixing 8 parts of lead, 15 of bismuth, 4 of tin, and 6 of cadmium, an alloy is obtained which melts at 68°, although none of its components melts below 200°. By thermal examination the composition of the various substances which are formed in the alloy may be deduced.

Information may be also obtained as to whether the alloy contains or is capable of forming a definite chemical compound by comparing the solidifying points of various alloys.

Thus, if small quantities of another metal are contained in any metal, the solidifying point of the latter will generally be lowered. On gradually adding further larger quantities of the second metal, the solidifying point will be further lowered until a minimum is reached, called the *eutectic* point, and up to this point there has been no chemical combination, because such combination would, on the other hand, raise the solidifying point. Those metals which do not form chemical compounds, but which form mixed crystals (p. 116) varying continuously in composition as the proportion of the components is varied, do not show minimal melting-points, that is, eutectic points, but the rise or fall of the temperature of solidification follows a continuous curve, rising or descending according to the metal which predominates at the beginning. In the preceding case, on the other hand, in which a eutectic point was found, we have an indication that these two metals are able to combine in definite proportions to form true chemical compounds. Thus, on continuing to increase the quantity of the second metal after attaining the eutectic point, the temperature of solidification steadily rises until a maximum is reached, and at this point the two metals form a chemical combination of definite formula. If now the quantity of the second metal is still further increased, the temperature of solidification is lowered because we have an *alloy* between the compound already formed and the excess of the second metal. A further minimum melting-point, that is, a new eutectic point (eutectic alloy), will again be obtained, but on continuing the addition of the second component, the melting-point will rise again until it reaches the melting-point of the second metal. Sometimes the two metals are able to form several successive chemical compounds, and then before the melting-point of the second metal is reached further maximum and minimum melting-points are traversed.

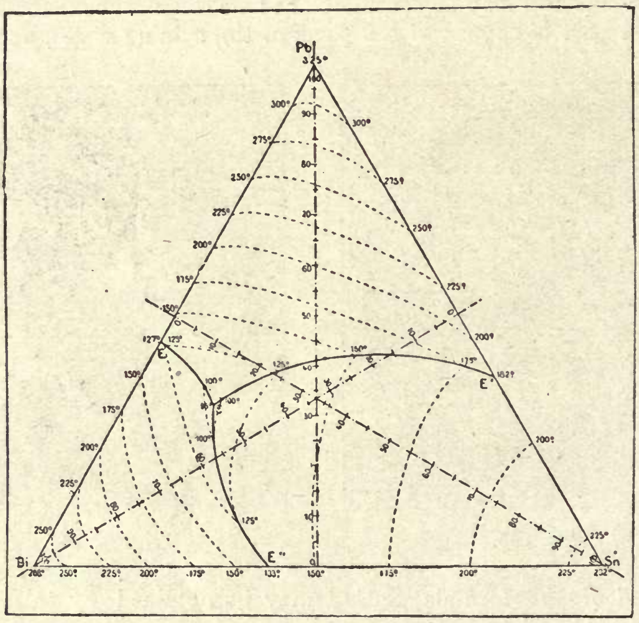


FIG. 205.

When two metals do not form compounds or even mixed crystals, then the *melting-point curve* may descend without passing through a true eutectic point, but will then rise continuously until the melting-point of one of the metals is reached.

The following alloys, which consist of true chemical compounds, are well known: $SnCu_3$, $PtHg_2$, PtZn, $PtSn_4$, Al_3Mn, Zn_3Hg, Cd_3Tl, Hg_6Na, and Hg_2Na.

In 1908 Tammann published the results of a complete study of more than 150 binary alloys.

In Figs. 205 and 206 we show a diagram in plan and in relief of the melting-points with the relative eutectic points of alloys of lead, tin, and bismuth.[1] Other diagrams and micrographs of metallic alloys are shown in the chapter dealing with iron and the steels.

The coefficient of elasticity of an alloy is generally equal to the mean of those of its constituent metals, and is the larger the more fine and homogeneous its grain.

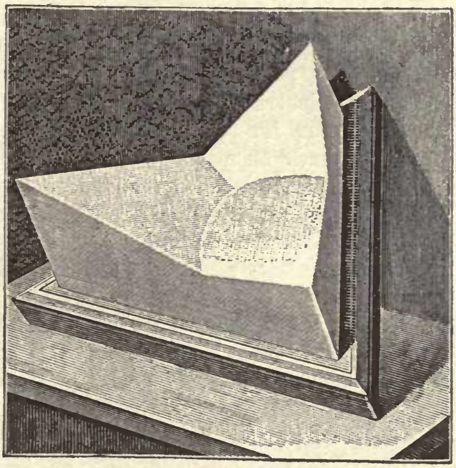


Fig. 206.

When an alloy is melted and allowed to cool slowly, certain of its components sometimes separate, forming solid layers of different composition. This phenomenon is called *liquation*; the Germans call it "*Saigerung*."

The chemical behaviour of an alloy is sometimes very different from that of its components. Thus an alloy of 56·5 per cent. of copper and 43·5 per cent. of zinc is not attacked by nitric acid, whilst copper or zinc alone is rapidly dissolved; further, an alloy of gold and silver containing less than one-third of silver is insoluble in HNO_3, whilst free Ag is soluble; also platinum is not soluble in nitric acid, whilst an alloy of platinum and silver dissolves completely.

The alloys of other metals with mercury are called *amalgams*.

---

[1] A diagram of fusibility for alloys of three metals (Pb, Sn, and Bi — anti-friction metal) may be represented as in Fig. 205, in which the vertices of an equilateral triangle correspond with the respective pure metals. The proportion of each metal which enters into an alloy of any definite melting-point is indicated by the line which forms the height of the triangle corresponding with the vertex of that particular metal. The sides of the triangle show the binary alloys, and all the internal points correspond with ternary alloys.

The melting-points of the ternary alloys may be represented by dotted curves which unite all the alloys of varying composition solidifying at the same temperature. Generally these curves form triangles of which the angles are arranged along three lines, E_ϵ, E'_ϵ, E''_ϵ, corresponding with the relative temperature minima. These three lines meet at a single point, ϵ, representing that alloy of the three metals which has the lowest melting-point.

In Fig. 206 the diagram of the preceding Figure is indicated in relief, and comprises all the alloys which can be formed from the three metals mixed in varying proportions. The three extreme highest points correspond with the melting-points of the respective pure metals. The surface which starts from these points is divided into three slopes separated by three depressions or valleys, which represent the lines of relative eutectic points converging towards the absolute eutectic point. In each of these three regions, on cooling, the pure metal which corresponds with the vertex of that region gradually separates in the solid state; along the relative eutectic lines the binary alloys of the metals corresponding with the two adjacent regions separate on cooling, and at the absolute eutectic point, which corresponds with the cryohydric point of salt solutions, etc., the whole of the ternary alloy solidifies on cooling. It is evident that in order to prepare such a diagram or model, numerous exact determinations are necessary, these then giving complete and exhaustive information on everything which can be done with an alloy of the three metals.

Fig. 203 is a microphotograph of one of the alloys in which the pale crystals of bismuth, which have separated between 175° and 125°, are clearly evident. Round each crystal one sees crystals of bismuth or tin deposited along the relative eutectic lines between 125° and 96°. The black part of the figure represents the homogeneous ternary alloy of the three metals corresponding with the absolute eutectic temperature. In Fig. 204, on the other hand, we see the angular crystals of antimony.

These crystals are of very great importance in alloys which are used for bearings for machinery, because only the softer portions of the alloy remain in a condition to be slightly adherent to the shafting, whilst the points of contact which carry the weight of the whole shaft revolving in the bearings are formed by these harder crystals, which present a minimum of surface and thus give a minimum amount of friction.

ELECTROCHEMISTRY

This branch of chemistry has acquired great importance on account of its practical applications in recent years. In many countries the importance of electrochemical industrial processes has been exaggerated and will lead to bitter and disagreeable and even costly disappointments. It is not to be denied that present-day electrochemical industry cannot afford to pay for expensive electrical energy, and that sometimes a price of only £2 or £2 8*s*. per h.p.-year for this commodity is too expensive, especially for certain products made on a large scale and sold at a low price.[1]

It is also necessary to remember that in Italy, where fuel is scarce, certain interests are always ready to buy electrical energy for transformation into light and power, even at a price of £6 to £8 or even £12 per h.p.-year, whilst in some countries abundant supplies of electrical energy cost only £1 to £1 8*s*. per h.p.-year.[2]

Under these conditions, it cannot be advantageous to develop electrochemical industries in all localities. It is not, however, impossible that in the future, when the yields and the production of electrical energy have been improved, the electrochemical industry will acquire much more importance than can at present be foreseen.

Many chemical phenomena are closely connected with electrochemical phenomena. It will suffice to mention the electrolytic dissociation of many substances when dissolved in water, such as salts, acids, bases, etc., and also many chemical reactions occurring under the influence of the electric current. Volta's cell was the first demonstration of the transformation of chemical into electrical energy, and a similar phenomenon is easily produced under the most varied chemical conditions (*see below*, Daniell's Cell). Volta actually believed that with his cell he had discovered a new infinite source of gratuitous energy with which it would be possible to produce perpetual motion without any corresponding

---

[1] Undoubtedly remunerative are the following industries: accumulators, which are produced to the value of £3,000,000 per annum; electro-deposition, which requires annually 15,000 tons of metals; electrolytic copper, which constitutes three-fourths of the American output and one-half of the world's output; electrolytic gold and silver, valued at £4,000,000 per annum; aluminium, all produced in the electric furnace with a purity attaining 99·7 per cent.; aluminothermic welding (*see* Aluminium); sodium, potassium, calcium, caustic soda and potash (and chlorine), which use 50,000 kilowatts; electrolytic hydrogen; electro-osmotic purification of clay for earthenware; phosphorus, ferro-tungsten, ferro-chrome, ferro-silicon, steel, synthetic nitric acid, carborundum, quartz, calcium carbide and cyanamide, aluminium nitride, chlorates, etc. All these industries absorb already about 1,000,000 kilowatts.

[2] The available water-power (h.p.) and that utilised in 1911 in different countries are approximately as follows:

	Available	Utilised	Percentage utilised
England	963,000	80,000	8·3
Germany	1,425,000	445,000	31·2
Switzerland	1,500,000	380,000	25
Spain	5,000,000	300,000	6
Italy	5,500,000	565,000	10·2
France	5,857,000	650,000	11·1
Austria-Hungary	6,460,000	515,000	8
Sweden	6,750,000	550,000	8·2
Norway	7,500,000	920,000	12·3
Total for Europe	40,955,000	4,405,000	10·6 (mean)
United States	26,736,000	4,016,000	15
Canada	17,764,000	1,013,000	8·2

consumption of energy. The law of the conservation of energy was not then known, and it was only much later that it had to be admitted that the electrical energy of the Volta cell was provided by energy resulting from a chemical reaction. In order to be able to study the relation between phenomena of these two kinds, it is necessary to be able to compare them quantitatively in terms of the same unit of measurement, and to know the various units used; among the most important of these for our purpose are the following—

The UNIT QUANTITY OF ELECTRICITY is the INTERNATIONAL COULOMB, and it is found experimentally that 96,540 coulombs are required to evolve 1·008 grms. of hydrogen from an electrolyte, such as acidified water.

An electric current which transports one coulomb per second has an intensity of one ampère, so that a current of one ampère carries in one hour a quantity of electricity equal to 3600 coulombs. The INTERNATIONAL AMPÈRE is the unit of current strength. If we wish to understand the significance of this current strength a little more clearly, we may compare it with a current of water which we will suppose to have a value of 1 when it transports, for example, 500 litres of water per second. The strength of this current will be doubled, that is, its velocity will be doubled, if it transports 1000 litres of water per second, and it will be trebled if it transports 1500 litres per second, the section of the outlet remaining constant.

A current of 1 amp. strength, in order to develop 1·008 grms. of hydrogen, must pass through the electrolyte for 96,540 seconds, that is, 26 hours and 49 minutes, because this current transports 1 coulomb per second.

The work produced by an electric current does not depend on the intensity only, but also on the tension or difference of potential of the current itself.

This tension may be compared, up to a certain point, with the height at which a given quantity of water is stored; the work which it produces in falling then varies with the *head* of water.

In order that a current may pass along a conductor (hydraulic or electric), it is necessary that a difference of levels should exist, and the work produced by the same quantity of electricity will be the greater the greater the potential difference or electrical level between the extremities of the conductor. This potential difference is the *electromotive force* of the current, and the practical unit of electromotive force is given by the potential difference which exists at the extremities of a conductor which has a resistance of 1 ohm (*see below*), and is traversed by a current of 1 amp.; this tension is equal to 1 (INTERNATIONAL) VOLT.

If we pass the same current through solutions of various salts, such as copper sulphate, zinc sulphate, silver nitrate, etc., then after a certain time 31·8 grms. of copper will have been deposited and at the same moment 32·7 grms. of zinc and 107·92 grms. of silver will have been deposited in the other voltameters. We see immediately that these weights represent exactly the equivalent or combining weights of these metals, and thus it is possible to measure the intensity of a current by weighing the quantity of material which is deposited at the electrodes in unit of time, and it has thus been found experimentally that a current of 1 amp. in one second deposits exactly 1·1175 mgrms. of silver, or 0·0104 mgrm. of hydrogen, or 0·6589 mgrm. of copper from a cuprous salt, or 0·3290 mgrm. of copper from a cupric salt, 0·3385 mgrm. of zinc, etc., and these quantities are in the same ratios to one another as the respective combining weights (p. 21); we may also measure the quantity of hydrogen gas evolved by 1 amp. in a voltameter containing dilute sulphuric acid.

These facts, which were studied by Faraday in 1833, led to an important and universal law called by his name, according to which, under equal conditions, the quantity of matter separated is exactly proportional to the current strength, and the same current passing through several separate electrolytes deposits from each quantities of matter which are in the same ratio as their equivalent or combining weights.

The work done by a continuous current per second is measured by the product of the current strength in ampères, and its potential difference in volts. The product of 1 amp. and 1 volt is 1 watt, which is thus the unit of measurement of electrical energy. One watt corresponds with 10^7 ergs per second, that is, 1 joule per second (p. 61); thus it is almost equal to the work produced by 100 grms. of water falling from a height of 1 metre.

Since this value is small, the kilowatt (kw.) = 1000 watts = 10^{10} ergs per second, that is, 1 kilojoule per second, is used in practice, and a horse-power corresponds with 736 watts.[1]

From these data it is easy to calculate the electrothermic equivalent, knowing that a calorie corresponds with 41,800,000 ergs (p. 61); thus the work produced by 1 watt per second corresponds with $\frac{10^7}{41,800,000} = 0{\cdot}2391$ cal. It is thus possible to calculate the *electrochemical equivalents,* as we have found above that 96,540 coulombs correspond with 1·008 grms. of hydrogen or 107·938 grms. of silver (the chemical equivalents or combining weights expressed in grams); thus one coulomb corresponds with 0·0011181 grm. silver.

An electric current passing through a conducting wire or a solution encounters a certain resistance which may be compared with the resistance encountered by water flowing through a tube, a resistance which increases with the length of the tube and decreases with increase of its cross-section.

The unit of resistance is the INTERNATIONAL OHM, which represents the resistance offered to the passage of a constant current by a column of mercury 106·3 cms. long and of a weight of 14·4521 grms. at 0°, the uniform cross-section thus resulting being 1 sq. mm.

The electrolytic process depends on the current strength, I, which, according to Ohm's law, is found by dividing the electromotive force, E, by the resistance, R—$I = \frac{E}{R}$.

The total resistance of a cell is made up of the sum of its internal resistance, R_1, and the resistance of the external circuit uniting the two poles, R_2, so that $I = \frac{E}{R_1 + R_2}$.

If, for example, we wish to calculate the current strength, I, passing through a system in which there is an electromotive force, E, of 3·4 volts, when the circuit is open, with an internal resistance, R_1, of 0·6 ohm and an external resistance of the circuit uniting the two poles, $R_2 = 4$ ohms, then on applying the general formula, we find

$$I = \frac{E}{R_1 + R_2} = \frac{3{\cdot}4}{0{\cdot}6 + 4} = 0{\cdot}74 \text{ ampère.}$$

If the electromotive force, E (voltage), of a source of electricity remains constant, the current intensity (ampèrage) may be modified by varying the resistances, R_1 and R_2, and since the resistance of a homogeneous wire is proportional to its length, l, and in inverse proportion to its cross-section, s (sq. mm.), the resistance of any conductor (rheostat) can be calculated thus: $R = \frac{\rho l}{100 s}$ ohms, where ρ is a constant factor (*specific resistance*, or resistivity, in microhms) which depends only on the nature of the conductor, and is defined for any substance as the resistance of a length of 1 cm. of 1 sq. cm. cross-section. In the case of copper, $\rho = 1{\cdot}584$ millionths of an ohm. If ρ is the specific resistance of a substance, then $\frac{1}{\rho}$ is its *specific conductivity*, which in the case of metals increases with

---

[1] *Equivalence of energy units:*

	Erg.	Kilogram metre	H.P.-hour	Watt-hour	Kilowatt-hour	Calories
Erg. . .	1	$1{\cdot}02 \times 10^{-8}$	$377{\cdot}8 \times 10^{-16}$	$277{\cdot}8 \times 10^{-13}$	$277{\cdot}8 \times 10^{-16}$	24×10^{-12}
Kilogram-metre	$9{\cdot}81 \times 10^{7}$	1	$370{\cdot}3 \times 10^{-8}$	2725×10^{-6}	2725×10^{-9}	0·002345
H.P.-hour .	$2646{\cdot}81 \times 10^{10}$	270,000	1	736	0·736	635·5
Watt-hour .	3600×10^{7}	367	$1{\cdot}359 \times 10^{-3}$	1	10^{-3}	0·864
Kilowatt-hour .	3600×10^{10}	367,000	1·359	1000	1	864
Calorie . .	4166×10^{7}	425	1574×10^{-6}	1·1574	11574×10^{-7}	1

fall of the temperature, whilst in solutions it generally increases as the temperature rises.[1]

ELECTROMOTIVE FORCE OF METALS; VOLTAIC SERIES OF THE ELEMENTS

If a zinc plate is immersed in a solution of copper sulphate copper is immediately deposited on the zinc, whilst a part of the latter passes into solution with formation of zinc sulphate.

This phenomenon is due to the fact that the electric charges of the copper ions are given up to the zinc plate, which then liberates zinc ions charged with electricity, these in presence of SO_4'' anions replacing the copper forming zinc sulphate. Thus the process continues with deposition of copper ions and formation of zinc ions. Although there is thus an exchange of electric charges, we cannot detect an electric current in the liquid because this continual transformation occurs at all points inside the liquid. If, on the other hand, we arrange the experiment in another manner, *i.e.*, as a Daniell cell (Fig. 207), we may study this phenomenon more closely; *K* is an open copper cylinder immersed in a pot, *P*, of porous earthenware, which contains a solution of copper sulphate and retains it, but allows the current to pass. *Z* is an open cylinder of zinc, immersed in a glass vessel which contains zinc sulphate. If the copper cylinder is united with the zinc cylinder by means of a metallic

---

[1] The following table gives the resistivity ρ in microhms and its temperature coefficient for a number of metals and alloys.

	ρ in microhms at 0°	Temperature coefficient between 0° and 100°
Aluminium, 99·60 % pure	2·444	0·00392
,, 99 % pure	2·563	0·00423
,, 97·5 % (2·26 % Cu, 0·24 % Fe)	3·820	0·00435
,, 94·4 % (3 % Cu, 0·25 % Si, 0·25 % Fe, 1·5 % Zn)	3	—
Silver	1·468	0·00400
Pure soft iron, reheated	9·065	0·00625
Ordinary iron wire	13·906	0·00426
Magnesium	4·355	0·00381
Nickel	12·323	0·00622
Gold	2·197	0·00377
Lead	20·380	0·00419
Platinum wire, diam. 0·026 to 0·0079 cm. about	10·935	0·00360
Electrolytic copper, reheated	1·561	0·00428
Tin	13·048	0·00440
Zinc	5·751	0·00406
Steel in wire	15·803	0·00390
,, Manganese (12 % Mn)	67·148	0·00127
,, Nickel (4·35 % Ni)	29·452	0·00201
Ferro-nickel	78·3	0·00093
Phosphor-bronze, wire telegraph	1·6	0·00394
telephone	5·6	0·00394
Silicon-bronze, wire telegraph	1·7	0·0037
telephone	3·84	0·0023
Bronze (2 % Sn)	4·57	0·00152
,, (10 % Al)	12·31	0·00105
Alloy, 70 % Cu, 30 % Mn	100·6	0·00004
,, 73 % Cu, 24 % Mn, 3 % Ni	47·7	0·00003
,, 75 % Cu, 25 % Ni	34·2	0·00019
,, 87 % Cu, 6·5 % Ni, 6·5 % Al	14·912	0·00064
Argentum, 60 % Cu, 25·5 % Mn, 14 % Ni, 0·3 % Fe	29·982	0·000273
Alloy, 1 Pt, 2 Ag	31·582	0·00024
,, 4 Pt, 1 Ir	30·896	0·00082
,, 9 Au, 1 Ag	6·280	0·00124
,, 94 % Al, 6 % Cu	2·904	0·00381
,, 97 % Cu, 3 % Al	8·847	0·00089

wire, *L*, deposition of copper immediately commences on the cylinder *K*, and simultaneously the corresponding quantity of zinc dissolves in *Z*. If we insert a current indicator in the wire circuit, we are able to detect an electric current passing through it in the direction from the copper to the zinc in the external circuit, that is, in the wire connecting the two poles, and consequently from the zinc to the copper inside the cell. The copper is thus the cathode and the zinc the anode. By means of an electrometer we may also observe that the zinc pole has a potential (voltage) higher than that of the copper pole, and thus the current passes from the former to the latter inside the liquid in order then to continue from the copper to the zinc in the external circuit. The potential difference between the two metals remains constant even if the surface and the distance between the electrodes are varied, and within certain limits even when the nature of the anion is varied. If one of the metals and the corresponding salt are replaced by another metal, which has a distinct, definite and constant potential, the difference of potential between the two metals of the elements in the Daniell cell remains constant under all circumstances. Each metal has a constant characteristic potential difference with respect to any other metal, this being called the electro-motive force of the metal.

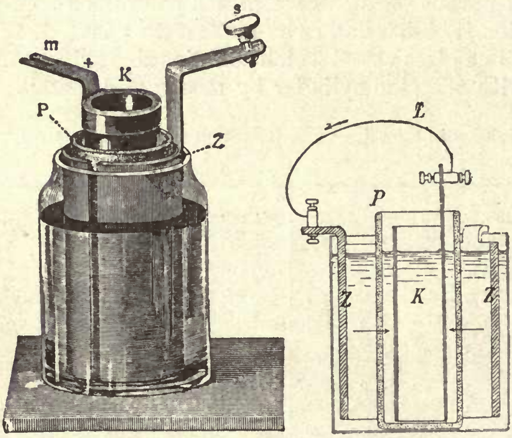


FIG. 207.

The metal of higher potential acts as a precipitant, passing into solution, becoming oxidised and acting as an anode (for example, zinc), whilst the precipitated or reduced metal acts as a cathode or negative pole to which the metallic cations pass (for instance, copper). It is thus possible to establish voltaic series, that is, to arrange the metals in a series in which one metal functions as precipitant or anode compared with another of higher potential which is precipitated in turn as cathode by another metal of still higher potential; thus, for example, cadmium precipitates metallic copper from copper sulphate, forming cadmium sulphate, but zinc precipitates cadmium from cadmium sulphate, etc.

By Faraday's law a certain quantity of zinc always produces the same quantity of electricity and precipitates different quantities of other metals in proportion to their equivalents, that is, it liberates an equal number of their ions. In order to separate, for example, different weights of cadmium and copper, a given quantity of zinc (corresponding with a definite quantity of electricity) must necessarily perform different amounts of electrical work, but the quantity of electricity being constant, it must act with different potentials in the case of two different metals, in exactly the same way as, in order to produce different amounts of work with the same quantity of water, it is necessary to allow it to fall from different heights.

For a silver-zinc couple there is a potential difference of 1·57 volts.
„ copper-zinc „ „ „ „ 1·10 „
„ cadmium-copper „ „ „ 0·35 „

In order to obtain the relative values of the potentials of the elements it is necessary to choose as an arbitrary zero the potential of any one element, from which we can then calculate the values of the others; if, for example, we take the value for zinc as zero, then the potential of silver will be 1·57, that of copper 1·10, that of cadmium 0·35. Starting from a zero which is not that of zinc, it has been possible to determine the tensions of all the metals, and we can thus establish the following electrochemical series of the elements which commences with the electropositive alkali metals and becomes more negative as we approach the non-metals up to fluorine.[1]

	Volts.		Volts.		Volts.
Cs	+	Tb	+ 0·11	As	− 0·55
Rb	+	Fe	+ 0·09	Cu	− 0·59
K	+	Co	− 0·02	Hg	− 1·03
Na	+	Ni	− 0·02	Ag	− 1·06
Mg	+ 1·24	Sn	− 0·09	Pd	− 1·07
Al	+ 1·03	Pb	− 0·10	Pt	− 1·14
Mn	+ 0·82	H	− 0·25	Au	− 1·36
Zn	+ 0·51	Sb	− 0·38	⋮	
Cd	+ 0·16	Bi	− 0·50	F	—

This electrochemical series is interesting from various standpoints; thus, the more electropositive metals are able to separate those which are less electropositive or more electronegative from solutions of their salts. Also those metals which are more electropositive than hydrogen have a solution tension greater than that of the H ions, and evolve hydrogen from dilute acids, whilst this cannot occur with those elements which are more electronegative, that is, which have a smaller potential. Thus copper and mercury do not evolve hydrogen with acids, and mercury is purified in practice by washing it with nitric or sulphuric acid because the impurities consisting of other metals dissolve rapidly in these acids. It also explains why it is not possible to transform copper directly into sulphate by the action of sulphuric acid, so that in order to obtain this salt it is necessary first to oxidise the copper. It also explains why copper is frequently used industrially for the construction of the most varied apparatus to resist the action of acids (in dyeing, sugar-refining, etc.).

We may also infer *a priori* how metallic alloys or metallic coatings, such as galvanised iron wire, tin-plate, etc., will behave in presence of an electrolyte or even in presence of rain water, which always contains small amounts of salts and of carbon dioxide in solution. In the case of "galvanised" (zinc-covered) iron wire, the zinc will go into solution (become oxidised) but not the iron, even though the latter is partially laid bare; whilst, on the other hand, tin-plate will easily form iron rust although well covered by tin at certain points, because the potential of the iron is higher than that of the tin, and it will therefore readily go into solution and become oxidised.

These theoretical deductions are strictly confirmed in daily practice.

ELECTROLYSIS : PRIMARY AND SECONDARY PRODUCTS. When a sufficiently concentrated solution of sulphuric acid is decomposed by electrolysis, at the anode, instead of the formation of oxygen and repeated regeneration of sulphuric acid occurring in the case of slightly acidified water, persulphuric acid and oxygen are formed through the condensation of two SO_4 anions with 1 mol. of water :

$$2(SO_4) + H_2O = O + H_2O_8S_2.$$

Those products of electrolytic decomposition which result directly from the ions are called primary products. Thus, in the case of HCl the primary products of the electrolytic dissociation are hydrogen and chlorine formed from the H and Cl ions. In the dissociation of sulphuric acid the oxygen may be considered as a secondary product of the electrolysis

---

[1] *Translator's note.*—In this series the *electropositive* elements, *i. e.*, those with the (+) sign, are those which form the *negative* pole of a cell, and *vice versa*, as the more positive ions travel through the internal circuit *with* the current.

because it is formed by the interaction of one of the ions with another substance, water. When HCl is electrolysed in very dilute solution oxygen is formed instead of chlorine at the anode as a secondary product, because $2Cl + H_2O = 2HCl + O$, and thus one may have both primary and secondary decomposition of water. In the electrolysis of concentrated solutions of NaCl, the Cl anion is carried to the anode where it escapes as molecular chlorine, but at the cathode metallic sodium is not formed, but hydrogen instead, because the metallic Na cation decomposes water as soon as it is formed ($Na + H_2O = NaOH + H$). In this case Na is a primary product and H and sodium hydroxide secondary products.

In order to separate the ions from an electrolytic solution at the cathode and the anode, it is necessary to use an electromotive force which increases with increase of the solution tension of the two kinds of ions, and with decrease of their osmotic pressure.

Therefore, in order to separate metals electrolytically it is necessary to take into account the potential difference at the electrodes and not merely the current intensity. In a solution containing both zinc and copper ions it is possible to separate the copper alone by means of a current of low electromotive force, but with a current of higher electromotive force (greater difference of potential) zinc also may be separated.

The decomposition voltage of certain cations and anions referred arbitrarily to that of hydrogen, which is considered as zero, is the following: *Cations:* $Zn^{\cdot\cdot}$ + 0·770 volt; $Cd^{\cdot\cdot}$ + 0·420; $Pb^{\cdot\cdot}$ + 0·148; $Cu^{\cdot\cdot}$ − 0·320; $Ag^{\cdot}$ − 0·771. *Anions:* SO_4H' − 2·6 volts SO_4'' − 1·9; OH' − 1·68; Cl' − 1·417; O'' − 1·08; Br' − 0·993; I' − 0·520. From these data the decomposition voltages of the most varied electrolytes may easily be calculated. Thus, in order electrolytically to decompose zinc iodide of normal concentration, a voltage of 0·520 + 0·770 = 1·290 volts will be necessary, and for copper sulphate, 1·9 + 0·329 = 2·229 volts.[1]

In order to interpret the electrochemical phenomena which we have noted in the Daniell cell, that is, the potential difference which arises between a metal and a solution of a salt, Nernst compared it with the vapour pressure produced by a liquid in a closed vessel, a pressure which increases until equilibrium is attained with the vapour pressure of the liquid itself (*see* p. 85), or with the osmotic pressure which a salt exercises when dissolved in water, a pressure which increases with the quantity of the salt until it is in equilibrium with the solution pressure. Thus, each metal immersed in a solution has a tendency, which varies according to its nature, to give off ions to the solution. This electrolytic solution pressure is the greater the smaller the number of metallic cations already present in the solution, that is, the smaller the osmotic pressure of the dissolved cations. In reality, however, the number of cations which a metal gives up to a solution is extraordinarily small, because as these are positively charged and the metal remains negatively charged, it attracts these cations and equilibrium occurs when as many ions enter into solution as are deposited at any given moment. Since, however, the electric charge of the few metallic ions in solution is very large, a potential difference between the metal and the solution may be immediately observed, a difference which is constant for each individual metal. In the Daniell cell, we have a potential difference between each of the two metals and the respective solutions. The electromotive force of the Daniell cell depends not only on the solution pressure of each of the two metals, but also on the osmotic pressure of the dissolved ions of each metal, and since this pressure is almost equal for zinc

---

[1] The quantity of electrical energy necessary for the electrolysis of a substance may be calculated with a certain approximation from the thermal change, 1 watt-second corresponding with 0·24 gram-cal. Thus, in the electrolytic decomposition of sodium chloride, the thermal balance is as follows: $NaCl = Cl + Na - 96{,}400$ cals., but the sodium reacts with the water of the solution: $Na + H_2O = NaOH + H + 43{,}400$ cals., so that the final result is − 53,000 cals. Consequently, the decomposition of sodium chloride (58·5 grams) by an electric current into NaOH (40 grms.), H (1 grm.) and Cl (35·5 grms.) requires 53,000 cals., corresponding with 220,800 watt-seconds $\left(i.e., \frac{53{,}000}{0{\cdot}24}\right)$, and since 736 watts are equivalent to 1 h.p., it follows that 300 h.p. are necessary to decompose electrolytically 58·5 grams of NaCl per second. Since the energy per gram-ion is 96,540 ampère-seconds, the minimum decomposition voltage will be $\frac{220{,}800}{96{,}540} = 2{\cdot}3$. A great part of the voltage is, however, used in overcoming the resistance of the electrolyte, so that a voltage higher than the minimum is used. Consequently the current yield is lowered, and to make this loss as small as possible, the resistance of the bath is diminished by placing the electrodes as near one another as possible, by increasing their surface, and by using pure, concentrated and hot electrolytes.

and copper ions, whilst, on the other hand, metallic zinc has a solution pressure much greater than metallic copper, the current will pass from the zinc to the copper in the internal circuit and the zinc will remain negatively charged (negative pole), because it gives off positive cations. The copper, on the other hand, will be positive because positive copper cations are deposited on it. If we now diminish the osmotic pressure in the copper sulphate by diminishing the number of the $Cu^{\cdot\cdot}$ cations by addition of potassium cyanide, which forms less ionised, complex $Cu(CN)_2$ with $Cu^{\cdot\cdot}$, we shall increase the pressure of the copper solution and a larger number of cations will thus pass into solution until they reverse the direction of the current. The electromotive force of a galvanic cell and the electric current which is caused by it depend more particularly on the solution pressures of the two metals, and we may thus consider the cell as a machine in which free chemical energy is transformed into free electrical energy. The process may be represented by the chemical equation, $Zn + CuSO_4 = ZnSO_4 + Cu$, that is, the zinc which displaces the copper ions dissolves and becomes converted into ions, and, on the other hand, converts copper ions into neutral deposited copper: $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$.

The Daniell cell may be regarded also as a reversible cell, since, if a current is passed through it in the opposite direction, *i. e.*, from the copper to the zinc, the copper ions will pass into the solution, while those of zinc will be deposited.

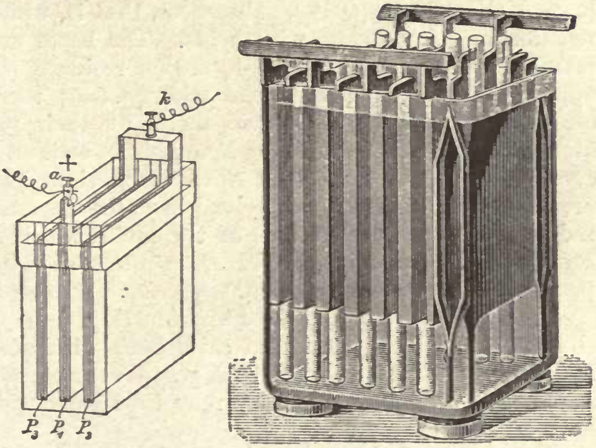


FIG. 208.

ACCUMULATORS. A very important type of reversible cell is that of the common lead-plate accumulator, which consists of a large number of porous leaden plates (Fig. 208) arranged parallel in a closed vessel containing very pure dilute sulphuric acid (20 to 25 per cent.). The lead plates are alternately covered with lead peroxide, PbO_2, and with lead sulphate, $PbSO_4$. All the plates (P_1) covered with the peroxide are connected with one another and form an anode or positive pole, *a*, whilst those covered with lead sulphate, P_2 and P_3, are also connected together forming a cathode or negative pole, *k*. By passing a current in through the positive plate, through the acid and out at the negative plate, the lead sulphate on the latter is reduced to metallic lead, whilst a corresponding quantity of lead peroxide accumulates on the other plate; when hydrogen commences to be evolved from the lead plate and oxygen from that coated with peroxide, this indicates that the cell is charged, that is, it has stored up electrical energy (potential energy: *see* p. 4). This charge is retained for a long time, provided that the two poles are not brought into metallic connection; when this is done an electric current passes in the reverse direction, because the lead peroxide plate, by its solution pressure, liberates free negative ions of PbO_2'', which neutralise the positive ions of $Pb^{\cdot\cdot}$ formed by the plate of spongy lead, forming neutral molecules of PbO which combine with sulphuric acid and form lead sulphate, this being deposited on the cathodic plate until the accumulator is discharged. During charging the following chemical reaction occurs: $2PbSO_4 + 2H_2O = 2H_2SO_4 + Pb + PbO_2$, while during the discharge we have firstly: $PbO_2'' + Pb^{\cdot\cdot} = 2PbO$, and then $2PbO + 2H_2SO_4 = 2\ PbSO_4 + 2H_2O$.

Accumulators are of great practical importance because they allow hydro-electric energy to be stored at times when it would otherwise be lost, for example, at night, so that it may be used, when a large supply of current is required, to help the ordinary dynamo, which does not thus require to be so large because it can be built of a size proportionate only to the hydraulic power which can be utilised by day.

The Bunsen and Leclanché cells are irreversible cells having cathodes of zinc and anodes of carbon, and when a current is passed through them in the reverse direction they do not regain their original condition. All cells, however, are sources of electrical energy provided by reaction between ions, and in every chemical reaction it can be shown by suitable apparatus that an electrical current is produced if the substances and the solutions taking part in the reaction are kept separate; the ions of the one portion then pass on their electrical charge to the other electrode by means of the interpolar circuit, causing the formation of new ions which arise from the neutral metallic molecules or by the neutralisation of ions, already free, of opposite charge.

The valency of metals is well indicated by their oxygen compounds, in which the oxygen is always divalent, and thus the metals may be divided into 8 groups according to their valency. These groups are evident in the periodic system of the elements, which will be considered at the end of this volume. The metals form the following various forms of oxides commencing with the group of the monovalent metals and rising up to the metals with a valency of 8:

I	II	III	IV	V	VI	VII	VIII
K_2O	MgO	Al_2O_3	SnO_2	Bi_2O_5	CrO_3	Mn_2O_7	OsO_4

The hydroxides corresponding with the first two groups are strong bases [*e. g.*, KOH and $Mg(OH)_2$], substances, that is, which show a strongly alkaline reaction and form salts with acids. The bases are substances formed from metallic cations united with hydroxyl residues (OH anions) and have an opposite chemical action to the acids (p. 96); the acids, on the other hand, are characterised by their acid taste, by their property of reddening blue litmus solution and of evolving hydrogen in contact with almost all the metals even in the cold, especially with magnesium powder. The fundamental properties of bases when dissolved in water are due to the OH group (anion) independently of the nature of the metal which they contain, and the OH group in solutions of the bases is present in the state of free ions and produces the alkaline reaction.

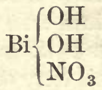
The hydroxides of the third and fourth groups possess both basic and acid characters, so that they form salts both with acids and with bases. The hydroxides of the fifth and seventh groups are not known, but the corresponding salts are well defined, and they may thus be considered as anhydrides which have an acid character.

The metals of the first and second groups form peroxides, such as Na_2O_2, BaO_2, etc., which are more highly oxidised and do not form salts, but easily lose one atom of oxygen when heated with oxy-acids, and form chlorine when heated with HCl; the peroxides of lead and manganese, PbO_2 and MnO_2, behave in the same manner.

Acids unite with bases (or oxides) to form salts with separation of water, and thus also the metallic oxides combine with acid anhydrides forming salts, but without separation of water. On dissolving metals in dilute acids, salts are also formed: $Zn + H_2SO_4 = ZnSO_4 + H_2$. However, the hydrogen of the acid which is thus evolved may sometimes act as a reducing agent on the acid itself. Thus, if we treat zinc with strong sulphuric acid, sulphurous acid and even hydrogen sulphide are also formed:

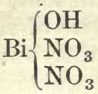
$$SO_4H_2 + H_2 = 2H_2O + SO_2, \text{ and also } SO_4H_2 + 4H_2 = 4H_2O + SH_2.$$

Nitric acid is also reduced in dilute solution; on the other hand, the acids of arsenic and antimony are more stable, and phosphoric acid still more so. In the formation of salts it is supposed that one or more atoms of the hydrogen of the acid are substituted by one or more atoms of a metal, but when the salt is formed by the action of an acid on a base which has more than one hydroxyl (OH) group [polyacid bases, such as $Bi(OH)_3$, $Pb(OH)_2$, $Zn(OH)_2$, etc., in contradistinction to polybasic acids] various types of salts may be formed, namely, *neutral salts*, in which all the OH groups of the polyacid bases are replaced by acid residues, or *basic salts,* in which only a part of the hydroxyl groups are replaced, as may be seen from the constitution of the following salts :



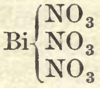
$\mathrm{Bi}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{NO_3}\end{cases}$

Dibasic bismuth nitrate



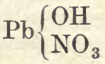
$\mathrm{Bi}\begin{cases}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{NO_3}\end{cases}$

Monobasic bismuth nitrate



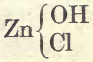
$\mathrm{Bi}\begin{cases}\mathrm{NO_3}\\ \mathrm{NO_3}\\ \mathrm{NO_3}\end{cases}$

Neutral bismuth nitrate



$\mathrm{Pb}\begin{cases}\mathrm{OH}\\ \mathrm{NO_3}\end{cases}$

Basic lead nitrate



$\mathrm{Zn}\begin{cases}\mathrm{OH}\\ \mathrm{Cl}\end{cases}$

Basic zinc chloride

FIRST GROUP OF THE METALS

ALKALI METALS

		(*a*) Atomic weight	(*b*) Specific gravity	(*c*) Atomic volume, c = a : b	(*d*) Melting-point	(*e*) Boiling-point.
Lithium . .	Li	7·00	0·59	11·9	180°	—
Sodium . .	Na	23·00	0·97	23·7	96°	742°
Potassium . .	K	39·10	0·87	45·0	62·5°	667°
Rubidium . .	Rb	85·45	1·52	56·1	38·5°	—
Caesium . .	Cs	132·81	1·88	70·7	26·5°	270°

As the atomic weight of these metals rises, so does the specific gravity, and even more so the atomic volume, whilst, on the other hand, the melting- and boiling-points become lower.

As in the case of the first group of non-metals—that of the halogens—the acid character is most pronounced, so also the first group of the metals has a more pronounced alkaline (basic) character than the others.

These metals oxidise in the air, and decompose water already in the cold, forming hydroxides[1] soluble in water and of strongly alkaline reaction, and not decomposed even on heating to redness. They have an alkaline reaction which is the greater the higher their atomic volume; lithium has the least markedly basic reaction. All the metals of this group are in general monovalent.

These elements may be divided, according to their chemical resemblances, into two sub-groups. Caesium, rubidium, and potassium have a more alkaline character and form comparatively insoluble tartrates and platinichlorides, which are used to separate them from the other sub-group, forming tartrates and platinichlorides which are more soluble. Also the carbonates and bicarbonates of Cs, Rb, and K are deliquescent, whilst those of sodium and lithium are not deliquescent in the air, and lithium carbonate is not very soluble in water.

POTASSIUM : K, 39.10

Whilst various potassium salts, such as the carbonate and nitrate, have been known since the most remote antiquity and have been long studied, free

---

[1] The heat of formation of the hydroxides dissolved in water, starting from the elements, is as follows : LiOH aq. = 491 Kj. (117,400 cals.); NaOH aq. = 467·8 Kj. (111,800 cals.); KOH aq. = 487 Kj., whilst the heat of formation of water from its elements is 286 Kj. Therefore, by the thermochemical law of the tendency to the formation of the most stable compounds with the maximum evolution of heat, the reason why the alkali metals decompose water forming the more stable alkali hydroxides is explained, and thus in general all metals which form hydroxides having a heat of formation greater than 286 Kj. are able to decompose water either on heating or in the cold, and do so the more energetically the greater the heat of formation of the respective hydroxides.

potassium was obtained for the first time by Davy in 1807 by decomposing potassium hydroxide (until then believed to be a simple substance) by means of a powerful electric current. Potassium in combination is abundantly and widely distributed in nature. It is found in all soils, as it is a constituent of many rocks, especially of felspar, a double silicate of aluminium and potassium, which by weathering, together with the other constituents of granitic rocks, is continuously forming constituents of new arable soil (soil may contain 0·1 to 0·2 per cent., and occasionally 0·4 to 0·5 per cent. of potash without being fertile, if the potash is not assimilable). It is thus found as a normal constituent of all vegetable organisms in the form of organic salts, and remains accumulated in the ashes of plants in the form of carbonate.

It is found as chloride and sulphate in sea water, 1 cu. metre of which contains 0·6 grm. of KCl, being carried into the sea by the rivers, which annually transport about 50,000,000 tons of potassium salts.

Free metallic potassium is prepared by heating a mixture of 30 parts of potassium carbonate with 13 parts of wood charcoal and 5 parts of gypsum: $K_2CO_3 + 2C = 3CO + K_2$.

The industrial methods are almost the same as those employed in the manufacture of metallic sodium, and will be described when speaking of that metal. At one time, tartar, that is, potassium bitartrate, which already contains sufficient quantities of lime, was used, being heated to a white heat in iron retorts, and the vapours of potassium condensed in vessels containing mineral oils (petroleum) which protected the potassium from oxidation or from catching fire in the air. Potassium carboxide, $(KOC)_6$, is generally obtained together with the potassium, and is explosive; it also obstructs the pipes and diminishes the yield. According to C. Winkler (1890) the formation of this product is avoided by reducing fused potassium hydroxide directly with red-hot magnesium:

$$KOH + Mg = MgO + H + K.$$

To-day, however, potassium is prepared mainly from potassium chloride by electrolytic means, by an industrial process analogous to that which we shall describe in the case of sodium. It appears, however (Ger. Pat. 140,737 of 1902), that pure potassium may be obtained at a low cost by distilling a mixture of potassium fluoride or fluosilicate with aluminium at a comparatively low temperature.

Potassium is purified by redistillation and by squeezing it through cloths.

It is a metal which, when fused out of contact with the air, has a silvery appearance and may crystallise in octahedra on solidifying. At the ordinary temperature it is soft and is easily cut with a knife. It has the specific gravity 0·87, melts at 58° and vaporises at about 720°, forming greenish vapours. It combines actively with oxygen, forming the oxide, which yields a hydroxide with water, and for this reason it readily decomposes many oxygen compounds and water itself. It is almost unaffected by perfectly dry oxygen, but a trace of water suffices to cause energetic reaction; in this case the water exercises a catalytic influence.

When a piece of potassium is placed on water, the latter is immediately decomposed with evolution of hydrogen, and so much heat is also generated that the potassium melts on the surface of the water and catches fire, together with the hydrogen.

It readily combines with the halogens, and metallic potassium on dissociating into ions evolves 259 Kj., which fact explains why it is possible to abstract chlorine from boron chloride and silicon chloride in the preparation of free boron and silicon. Potassium salts in general impart a pale violet-blue colour to the Bunsen flame.

There is no large demand for metallic potassium, and it is placed on the market in small balls under petroleum at a price of £1 8*s*. per kilo, whereas in 1865 the price was £10.

POTASSIUM SALTS AND FERTILISERS. At one time potassium salts were obtained from wood ashes which were produced more especially by the destruction of enormous Russian and American forests, but since Frank, in 1860, showed the extraordinary importance of the immense saline deposits stretching from the slopes of the Harz Mountains to the Elbe, from Magdeburg to Bernburg, and having their centre at Stassfurt (near Magdeburg),[1] almost all potassium salts have been prepared from the crude salts of these deposits and from those developed more recently in Alsace and Spain.[2]

---

[1] In 1837 the first shaft for the extraction of rock salt was sunk at Artern, and in 1839 another well was sunk at the same place, but at a depth of 581 metres the boring was stopped, since the rock salt was contaminated with potassium and magnesium salts which imparted to it a bad flavour. In 1851 von Carnalls started sinking two other shafts which occupied four years and reached the rock-salt layers, the contaminating magnesium and potassium salts being separated by hand and set aside as waste (Abraumsalzen), a quantity of 600 tons soon accumulating. The Inspector of Mines, Krug von Nidda, interested the manufacturers of chemical products in the utilisation of these residues for the recovery of the potassium chloride, and from this time (1861) date the studies and the first industrial experiments of Frank. In the Middle Ages and also later certain springs in the Stassfurt district were renowned for their medicinal properties.

[2] **Other Sources of Potassium Salts.** In 1912, near the bank of rock salt at Cardona, in the north of Spain, the discovery was made of a layer of carnallite, 80 metres thick, containing 20 per cent. of KCl, and of sylvine, 10 metres thick, containing 95 per cent. of KCl; these may have the same origin as the Alsace deposits, since they do not contain sulphates. This deposit appears to stretch with more or less intensity over an area of about 120,000 hectares, conceded in 1914 to various companies (Spanish, French, Swiss, German, and American).

In Chile, Lakes Pintados and Bella Vista (Tarapaca province), with an area of 4000 hectares, are covered with a saline crust 20 cm. thick, and containing 3 to 14 per cent. of KCl, while the waters contain 0·8 per cent. of KCl; this crust is renewed every 8 to 10 years. In 1905 the KCl in these crusts was estimated at 2,000,000 tons, and in 1915 an American company investigated them with a view to their industrial development.

Small quantities of potash salts (in Europe about 3000 tons) have for long been recovered from greasy wool (*see* Vol. II., "Organic Chemistry"), and about 20,000 tons from the residues from the alcoholic fermentation of beet molasses—after evaporation and calcination (*see later :* Potassium Carbonate).

Many attempts have been made to utilise felspathic rocks (leucite and orthoclase, which are aluminium and potassium silicates, and contain, on an average, about 10 per cent. of K_2O), by rendering the potash soluble in water. In 1904 Gibbs proposed to decompose the rock with hydrofluosilicic acid and then with sulphuric acid to give K_2SO_4. In 1907 Cushman electrolysed the powdered rock suspended in water and a little HF to obtain potassium and aluminium hydroxides. As early as 1856 Bickell suggested heating a mixture of felspar, coke, and natural phosphates. The Roman Sulphate Company endeavoured to obtain sodium aluminate and potassium carbonate by roasting leucite with sodium carbonate, hydroxide or nitrate and lime, a current of steam being passed through the mass at the end; finely powdered leucite containing 17 per cent. of K_2O is sold at £1 12*s*. per ton. In 1911 Thompson patented a process for preparing potassium sulphate by heating a mixture of felspar, sodium bisulphate, and sodium chloride to bright redness. For various reasons all these processes proved impracticable. The Bickell process was modified in different ways. When heated to redness, a mixture of 1 part of felspar, 0·5 of calcium phosphate, and 3 of lime yields a product which contains phosphates but little assimilable by plants, and at 1400° almost all the potassium volatilises, the same happening if calcium chloride is added to the mixture; the residue is simply a cement and the condensed volatile products contain K_2O or KCl. When tested in American cement factories in 1912–1915, this process also gave unfavourable practical results. When heated, alumite (double sulphate of aluminium and potassium) gives up water and SO_3, the residual potash alum losing more SO_3 at 700° and leaving a mixture of potassium sulphate and alumina containing 15·95 per cent. K_2O and 15·37 per cent. SO_3; it is, however, not convenient to lixiviate with water, and it is preferable to employ it directly as a fertiliser. According to Ger. Pat. 261,099 (1911) the potassium of leucite and phonolite is convertible into nitrate by boiling with concentrated calcium nitrate solution (*see below*). O. N. Witt (Norw. Pat. 20,306) heats felspar for 8 to 10 hours in an autoclave with milk of lime at 150° to 200°.

In 1914, Cushman and Coggeshall (America) proposed to recover the potash as chloride from the ground felspar by mixing the latter with quicklime, moistening the mass with concentrated calcium chloride solution and heating it to redness in a revolving furnace like those used for cement (*q. v.*); the roasted mass falls in lumps into vats of water, in which most of the chloride dissolves, the residue being washed with water and the wash water used for succeeding operations. The concentrated solution is evaporated in boilers by means of flue gases, the

The origin of the saline deposits of Stassfurt is explained in the following manner. Rain water dissolves potassium salts from the soil and the rocks, and those which are not absorbed by plants are carried out to sea. By the natural evaporation of the water of bygone seas (carved out of the ocean in the lower regions of Northern Germany), large deposits of salts were formed, arranged in the order of their solubility, sometimes in the pure state and sometimes as mixtures of salts well defined in relation to the chemical equilibria resulting from the prevailing conditions of concentration and temperature (varying between 25° and 73°).

The lowest strata of these deposits consist of sodium chloride (rock salt) and in some localities their thickness is more than 1000 metres. Above the sodium chloride, strata of carnallite, a double chloride of magnesium and potassium, $MgCl_2 + KCl + 6H_2O$, are found of a thickness of 20 to 40 metres. After the complete evaporation of these seas (calculated to have lasted at least 15,000 years), the carnallite would certainly be easily redissolved by rain water excepting where, through the action of the wind or through foldings of the earth's crust, these strata were covered by other strata of earth or rocks impermeable to water, which preserved them to the present time. Where, however, water was able to penetrate to the carnallite, this dissolved the magnesium chloride by preference and left the important deposits of *sylvine*, which consist of almost pure KCl and are very valuable. The water saturated with $MgCl_2$, on filtering through strata of gypsum, became saturated with calcium sulphate and then in contact with other salts of magnesium and potassium, such as carnallite, new salts were formed which collected as large deposits of *kainit* (to which Precht has attributed the formula, $MgSO_4$, K_2SO_4, $MgCl_2 + 6H_2O$, whereas van't Hoff, from crystallographic considerations, regards as more accurate the formula, KCl, $MgSO_4$, $3H_2O$).

The importance and great development of the potassium salts industry in Germany may be deduced from the following figures, which represent the annual production of the different crude potassium salts destined to supply the enormous demands of agriculture for this valuable and indispensable fertiliser.[1]

---

liquid paste obtained being taken to dryness in a revolving drum furnace. The dry mass, containing 70 to 80 per cent. KCl and 14 to 16 per cent. NaCl (the felspar contains about 10 per cent. K_2O and 1·5 to 2 per cent. Na_2O), is powdered, and is then ready for the market. Fractional recrystallisation of the crude chloride yields pure sodium and potassium chlorides. The cost price of this crude chloride (80 per cent. KCl), calculating a daily consumption of 300 tons of felspar at 4*s.* per ton, 60 tons of quicklime at £6, and 60 tons of calcium chloride at £1 9*s.* per ton, redemption of plant, etc., would be £6 5*s.* per ton, whereas Stassfurt chloride of the same grade would cost £7 10*s.* per ton in America. The extraction of the alkali is facilitated and the yields increased if the felspar, after being heated with lime and cooled, is hydrated with a little water, which is absorbed with heating and powdering of the mass, so that grinding is rendered unnecessary. This powdering is effected better in an autoclave at 4 to 5 atmos. for 4 hours with steam at high pressure.

According to Ger. Pat. 252,278 (1911), to separate the potassium salts from the sodium salts obtained on treatment of felspar, both are converted into nitrates by boiling with calcium nitrate, the calcium being separated as hydroxide along with various insoluble impurities (of Al, Si, Fe). Concentration of the filtered solution results in the separation first of potassium nitrate, which is washed on a centrifuge with water and a little nitric acid; when treated with KCl, the mother-liquors—containing $NaNO_3$ and a part of the KNO_3—yield fresh quantities of potassium nitrate (*see later:* Conversion Nitre).

The mother-liquors of sea-salt works contain appreciable proportions of potassium salts, and in France these are obtained in considerable amount from this source, various processes of treating the mother-liquors being in use.

The United States has developed the industry of potash salts obtained from marine algæ (*see* Iodine), and in 1916 the salts thus obtained corresponded with 1411 tons of K_2O. Large areas exist several square miles in extent, covered with algæ belonging to the family of the Laminariaceæ, the two commonest being *Nereocystis luetkeana* P. and R. on the north, and *Macrocystis pyrifera* Ag. on the south of the Pacific Coast; these algæ bear the name of kelp and give the best yields on lixiviation.

[1] The plants which fix most potash from the soil are the beet, potato, meadow grass, vine, olive, fruit trees, tobacco, etc., and in general these remove twice or thrice as much potash as phosphoric acid; at least 100 to 200 kilos of potassium sulphate or chloride per hectare should be returned to the soil per annum to maintain the fertility of the soil. Stable manure is too poor in potash salts. When cost of transport is not too high, kainit may be used in place of the more concentrated potassium salts. Kainit usually contains 13 to 14 per cent. of K_2O and costs one-fourth as much as the chloride; it is used in the proportion of 500 to 600 kilos per hectare and appears to exert also a favourable effect on weeds and insects, owing to the considerable amount of magnesium chloride it contains.

Year	Tons	Value £
1865	60,000	—
1875	300,000	—
1880	665,800	—
1885	1,027,000	1,280,000
1890	1,275,000	—
1895	1,600,000	—
1900	3,053,000	—
1904	4,085,000	2,400,000
1906	5,550,000	3,600,000
1908	6,100,000	—
1909	7,040,000	5,000,000
1910	8,161,000	—
1911	9,796,500	7,600,000
1912	11,070,000	8,800,000
1913	—	9,520,000
1914	—	7,760,000

In 1904, 1,906,000 tons of kainit were extracted, as well as 2,179,000 tons of other potassium salts—carnallite, schönite (K_2SO_4, $MgSO_4$, $6H_2O$) and sylvine, and in 1909 3,280,700 tons of carnallite and 344,750 tons of sylvinite. The statistics given for recent years indicate the total quantity of K_2O in the various potassium salts, the amount being 1,021,800 tons for 1912 and 1,126,000 tons for 1913.

Whereas in 1880, 57 per cent. of the potash salts extracted was employed for industrial, and 43 per cent. for agricultural purposes, in 1913 the respective percentages were 10 and 90.

The world's requirements of potassium salts could be satisfied by two-thirds of the works at Stassfurt, and since, further, other sources of potassium salts will be developed in other countries, it is easy to understand why the Syndicate is regulating the production with a view to preventing crises in the future. In the meantime more than two-fifths of the high grade salts are exported (in 1909, 148,500 tons to the United States—*see* Note—13,300 to Austria, 8,900 to Russia, 17,700 to France, 4130 to Italy, etc.),[1] whilst the lower

---

[1] The potassium salts were used in Germany and other countries in 1908 for the following purposes:

		For potassium carbonate and hydroxide	For conversion saltpetre	For potassium chromate	For potassium chlorate	For alum	For manures	For various purposes
		Tons	Tons	Tons	Tons	Tons	Tons	Tons
Potassium chloride of 80 per cent. strength	in Germany	78,425	20,158	678	517	—	100	5402
	in other countries	4,440	20,736	3,118	17,582	480	132,136	4750
Potassium sulphate of 90 per cent. strength	in Germany	—	—	—	—	494	92	2235
	in other countries	—	—	—	—	2,183	49,608	140

The output of 1,126,000 tons of K_2O in 1913 was consumed as follows: in Germany, 604,000 tons; United States, 248,295; Holland, 43,673; France, 42,437; Scandinavia and Denmark, 34,130; Austria-Hungary, 28,300; Great Britain and Ireland, 29,420; Belgium, 15,234; Russian Poland, 13,246; Russia, 4906; Italy, 7320; Spain, 8355; Switzerland, 3478; Baltic Provinces, 6415; Portugal, 1241; Luxemburg, 410; S. America, 2900; Australia, 2547; Balkan Countries, 198; Asia, 6713; Africa, 4370. In 1911 the United States imported from Germany 643,000 tons of crude potash salts, 229,000 tons of potassium chloride, and 144,000 tons of mixed potassium and magnesium sulphate.

The increase of the mean yield of the harvest in Germany from 1885 to 1910 as a result of intensified chemical fertilising is shown by the following figures, representing tons per hectare (2·47 acres):

	Rye	Wheat	Barley	Potatoes	Oats	Hay
1885	1·18	1·51	1·5	10·1	1·41	3·27
1910	1·67	1·99	1·95	13·9	1·92	4·34

grades, which could not bear freightage, are consumed in Germany, where in 1906 200,000 tons of *Abraumsalze,* valued at £1,520,000 were utilised. Several times, starting from 1876, syndicates of the potash factories have been formed for controlling the sale of the products of Leopoldshall, Stassfurt. In 1910 the Syndicate was reconstituted with sixty-five factories, only three taking no part. The convention should have lasted until 1915, but before that year it was prolonged till 1925.[1] Of the various functions of the Syndicate, great importance attaches to the spread of propaganda throughout the world with a view to extending the use of potash salts in agriculture and to lowering their price.

One of the most serious problems which has existed for many years in the neighbourhood of Stassfurt, where enormous quantities of various salts are treated, is the disposal of the waste liquors, which are rich more especially in $MgCl_2$, and, when introduced into water-courses, canals or ditches, filter through the soil to great distances and contaminate all the wells and sources of drinking water, destroying the fish and spoiling the water for cattle. In the treatment of carnallite alone, more than 1,500,000 cu. metres of these waters with 30 per cent. of salts are produced annually; after the bromine has been recovered from them, they are—provided that they cannot be passed into rivers—evaporated to dryness and the residual solid salt used to fill the galleries from which the potash salts were excavated.

It is of interest to note how this enormous quantity of agricultural potassium salts is distributed among different countries, and the following table shows the amount of such salts, expressed as K_2O, referred to 1000 inhabitants and to each square kilometre of cultivated land.

Country	Kilos of K_2O per 1000 inhabitants			Kilos of K_2O per square kilometre of cultivated land		
	1895	1901	1911	1895	1901	1911
Holland	515·6	1900·6	—	125·3	461·9	1695
Germany	1151·2	2638·5	8000	171	391·9	1200
Belgium	443·4	970·4	—	136	297·7	482
Sweden	1019·7	1874·6	—	145	266·6	490
Scotland	102·3	889·5	—	14	254·6	440
Switzerland	271	550	—	39·2	79·5	119
England	85	135·6	—	7	61·5	170
United States	465·7	1045·8	3200	24·1	54	86
Austria	41	130	—	5·6	17·8	107
France	130·7	163·2	—	13·4	16·8	80
Spain	20	139·4	—	1·3	8·5	44
Italy	28	41·7	—	4·3	1	38
Russia	4·5	20·1	—	0·2	—	13
Norway	—	—	—	—	—	397
Denmark	—	—	—	—	—	220
Ireland	—	—	—	—	—	138
Portugal	—	—	—	—	—	24

The characters of the different salts are as follows:

Commercial carnallite is in reddish-yellow, deliquescent, crystalline masses of the following mean composition: 15·5 per cent. KCl, 12·1 $MgSO_4$, 21·5 $MgCl_2$, 22·4 NaCl, 1·9 $CaSO_4$, 0·5 insoluble matter, 26·1 water.

Potassium chloride may be of 98 per cent. purity, and the NaCl present less than 0·5 per cent., whereas crude KCl may contain as much as 22 per cent. NaCl, and shows less than 2 per cent. of moisture and less than 0·5 per cent. of insoluble substances.

Kainit and hard salt form granular, crystalline masses of grey, yellow or reddish colour, with the mean composition: 19·4 per cent. K_2SO_4, 3·8 KCl, 13·4 $MgSO_4$, 9·9 $MgCl_2$, 35·1 NaCl, 2·5 $CaSO_4$, 1 per cent. insol. matter and 11·9 H_2O (it should contain less than 8 per cent. of

---

[1] By the law of 1910 regulating dealings in Stassfurt salts, these were divided into five groups, the prices for home consumption being fixed: I, Potassium chloride with at least 80 per cent. of KCl (*i. e.,* 50 per cent. K_2O); II, Potassium and magnesium sulphates, with at least 42 per cent. K_2O; III, Potash fertilising salts, with 20 to 22 per cent. or 30 to 32 per cent. or 40 to 42 per cent. K_2O; IV, Kainit, hard salt (mixture of sylvine, kieserite, and rock salt), and sylvinite, with 12 to 15 per cent. K_2O; V, Carnallite, with 9 per cent. or, of higher grade, with at least 13 per cent. K_2O.

The rapid increase of consumption in the United States is shown by the figures: £840,000 in 1900, £2,540,000 in 1910, and £3,040,000 in 1911.

In 1911 the world's consumption of potash salts from Stassfurt was 940,291 tons (calculated as K_2O), in 1912 1,000,000 tons (one-half of this being consumed in Germany), and in 1913 1,126,000 tons.[1]

POTASSIUM HYDRIDE : KH. This compound is one of the few hydrogen compounds of metals. It is a solid of silvery appearance and is obtained by passing a current of hydrogen over molten potassium at 300° to 400°. It is decomposed by water with evolution of hydrogen, catches fire spontaneously in the air, and when heated *in vacuo* first melts and then gradually dissociates as the temperature is raised above 200°.

If heated *in vacuo* in a closed vessel so that the evolution of hydrogen is hindered, this exercises a pressure which reaches 45 mm. at 330°, and prevents further dissociation. If the pressure is increased the reverse reaction occurs, that is, the free hydrogen acts on the potassium which has already been liberated and KH is again formed. Exothermic compounds generally behave in this manner, whilst in the case of endothermic compounds the products of decomposition or dissociation do not recombine under pressure.

POTASSIUM OXIDE : K_2O. This compound has only recently been prepared by heating a mixture of potassium nitrate and potassium in the proper proportions:

$$KNO_3 + 5K = 3K_2O + N.$$

It forms a grey crystalline mass which becomes yellowish in the air through formation of **Potassium Peroxide, K_2O_2.** It reacts energetically with water, with which it catches fire.

POTASSIUM HYDROXIDE : KOH (CAUSTIC POTASH)

This compound is prepared on the large scale by adding calcium hydroxide (milk of lime) to a boiling dilute solution of potassium carbonate, K_2CO_3, of 12° to 13° Bé.; $K_2CO_3 + Ca(OH)_2 = CO_3Ca + 2KOH$. The reaction is, however, reversible, and therefore in order to obtain a good yield the concentration and temperature must be maintained between certain limits. The

---

Cl, from the $MgCl_2$, soluble in 96 per cent. alcohol). The true composition of kainit is given on p. 530.

Sylvinite (mixture of sylvine, rock salt and a little kainit) contains on the average 28·3 per cent. KCl, 5·2 K_2SO_4, 3·6 $MgSO_4$, 1·8 $MgCl_2$, 51·3 NaCl, 1·8 $CaSO_4$, 4·2 insol. matter, and 3·8 H_2O; it should contain more than 12·4 per cent. K_2O.

Potassium sulphate: one grade has 90 per cent. K_2SO_4 (48·6 per cent. K_2O) with a maximum of 2·5 per cent. Cl, and another grade 96 per cent. K_2SO_4 (51·8 per cent. K_2O) with at most 1 per cent. Cl.

Potash fertilising salts are various mixtures of sulphates and chlorides of potassium, magnesium, sodium and calcium; they contain 15 to 40 per cent. K_2O.

Mixed potassium and magnesium sulphate contains at most 2·5 per cent. NaCl, a little $CaSO_4$, and about 0·5 per cent. of insoluble matter; it is calcined before being sold as fertiliser, or else used crystallised in alum works. It contains at least 48 per cent. K_2SO_4.

[1] **Potassium Salts and the European War.** During the European War the exportation of potassium salts from Germany ceased and caused a serious crisis in all hostile countries, being felt not only by agriculture, but also by the manufacture of explosives with a chlorate or perchlorate basis. Everywhere attempts were made to supply at least immediate needs, and in the United States five works were started to utilise the potash salts of the waters of the Nebraskan lakes, these on simple evaporation leaving a residue of the composition: 27·35 per cent. K_2O, 28·39 Na_2O, 22·44 CO_2 (of carbonates), 16·77 SO_3 (of sulphates), and 2·02 Cl (of chlorides). The amount obtained in 1916 was 3623 tons (K_2O), to which were added 1678 tons obtained from the working of alumite and silicate rocks (but very little from leucite and felspar), 1411 tons from the ashes of marine algæ, 374 tons from vegetable ashes (pearl ash), and 1674 tons from molasses residues. Altogether, the United States produced in 1916 32,382 tons of various potassium salts with a mean strength of 27 per cent. (only 3000 tons in 1915).

In Italy recourse was had to the potassium chloride of the Salt Plain of Ethiopia, this consisting of an ancient sea-bed, now separated from the Red Sea by a strip of sandy soil 60 to 70 kilometres wide. The lowest point of the Salt Plain is 100 metres below the level of the sea, and salt lakes form with heaps of salt at the vertices of which craters appear, these spasmodically erupting concentrated solutions of pure magnesium chloride, potassium chloride, etc. The potassium salt is found mixed with desert sand and at certain points is very pure (90 to 92 per cent., 1 to 2 per cent. NaCl, the remainder Fe_2O_3, sand, etc.), and in more extended areas it contains 65 to 75 per cent. KCl, 15 to 25 per cent. NaCl (for complete analysis, *see later :* Potassium Chloride).

Recovery of potash from olive residues in Italy has been suggested, but there is difficulty in dealing with small, scattered quantities.

solution of KOH is decanted from the insoluble calcium carbonate and concentrated in iron pans, the salts which are first deposited and which mainly consist of potassium carbonate and sulphate, being rejected.

The electrolytic preparation of this compound from potassium chloride in an analogous manner to the process which we shall describe for sodium hydroxide, has to-day been greatly developed; pure potassium chloride must be used, the presence of sodium chloride lowering the yields.

In Germany in 1903, 12,000 h.p. were employed for the production of 28,000 tons of electrolytic potassium hydroxide, and 48,000 tons of chloride of lime; 5000 tons of electrolytic sodium hydroxide and 12,000 tons of the corresponding chloride of lime were also produced.

PROPERTIES. Pure potassium hydroxide is a white crystalline solid which melts fairly easily at a dull red heat and evaporates unaltered at much higher temperatures. It absorbs water very energetically and is deliquescent in the air (table of densities of aqueous solutions given on p. 555).

It very readily absorbs carbon dioxide from the air, forming potassium carbonate. In aqueous solution it has a strongly alkaline reaction, and readily saponifies fats. It attacks the skin and many organic substances energetically, dissolving them. From a concentrated solution, a solid hydrate, $KOH, 2H_2O$, separates in the cold.

Potassium hydroxide readily reacts with the halogens:

$$6KOH + 6I = 5KI + IO_3K + 3H_2O.$$

When chlorine is passed into a cold solution of KOH, potassium hypochlorite, KClO, is formed; if the solution is hot, potassium chlorate, $KClO_3$, results.

Potassium hydroxide is easily dissociated in aqueous solution into the ions $K^{\cdot}$ and OH'. On pouring this solution into that of a neutral salt, such as $ZnSO_4$, which is dissociated into $Zn^{\cdot\cdot}$ and SO_4'', a zinc cation unites with the OH' anion and separates as the hydroxide $Zn(OH)_2$, because this is only slightly soluble. This reaction is general for all soluble salts of those metals which form only slightly soluble hydroxides. These general reactions of KOH are due to the OH' anion, and not to the cation $K^{\cdot}$, because on employing NaOH or RbOH, etc., the identical reactions due to the OH' anion occur and are common to all the hydroxides of the various alkali metals.

On evaporating solutions of KOH a solid mass is obtained, which melts easily and may then be formed into solid sticks if the fused mass is poured into cylinders of well-polished iron or into silver moulds (*see* NaOH).

APPLICATIONS AND PRICES. Potassium hydroxide is used in large quantities for the manufacture of soft soap and of the more refined soaps, which cannot be obtained with sodium hydroxide alone. It is also used in the preparation of oxalic acid and for preparing caustic lyes, although to-day it is replaced wherever possible by sodium hydroxide, which is cheaper.

Vessels in which KOH is kept must be closed hermetically so that it may not absorb H_2O and CO_2.

The fused commercial product containing 80 per cent. of hydroxide costs about £26 to £28 per ton, and that containing 90 per cent. of hydroxide £30 to £32. The pure product in sticks costs about £5 4*s*. per 100 kilos, and when purified with alcohol as much as £10. Solutions containing 50 per cent. of KOH are sold at £20 per ton. The strength is expressed as K_2O (*see* Caustic Soda).

In 1908 Germany exported 22,245 tons of potassium hydroxide valued at £389,280, and in 1909 27,477 tons.

The United States imported 4000 tons in 1910 and 3500 (£57,400) in 1911, although the Niagara Alkali Company produced 3000 tons in 1911, and in 1914 was made capable of an output of 10,000 tons per annum.

POTASSIUM CHLORIDE: KCl

This compound is found abundantly in the Stassfurt deposits as *sylvine* (also in Ethiopia, *see* pp. 533 and 536), or mixed with magnesium chloride as *carnallite*, $MgCl_2$, $KCl + 6H_2O$, which is ordinarily treated for the extraction of the chloride at a comparatively low cost, because it is more abundant. By treating it with a little hot water or with mother-liquors already saturated with $MgCl_2$, it is possible to separate the KCl, because the $MgCl_2$ is more soluble. Also by melting carnallite at 176° 75 per cent. of the potassium chloride may be obtained almost pure in the solid form on cooling.[1]

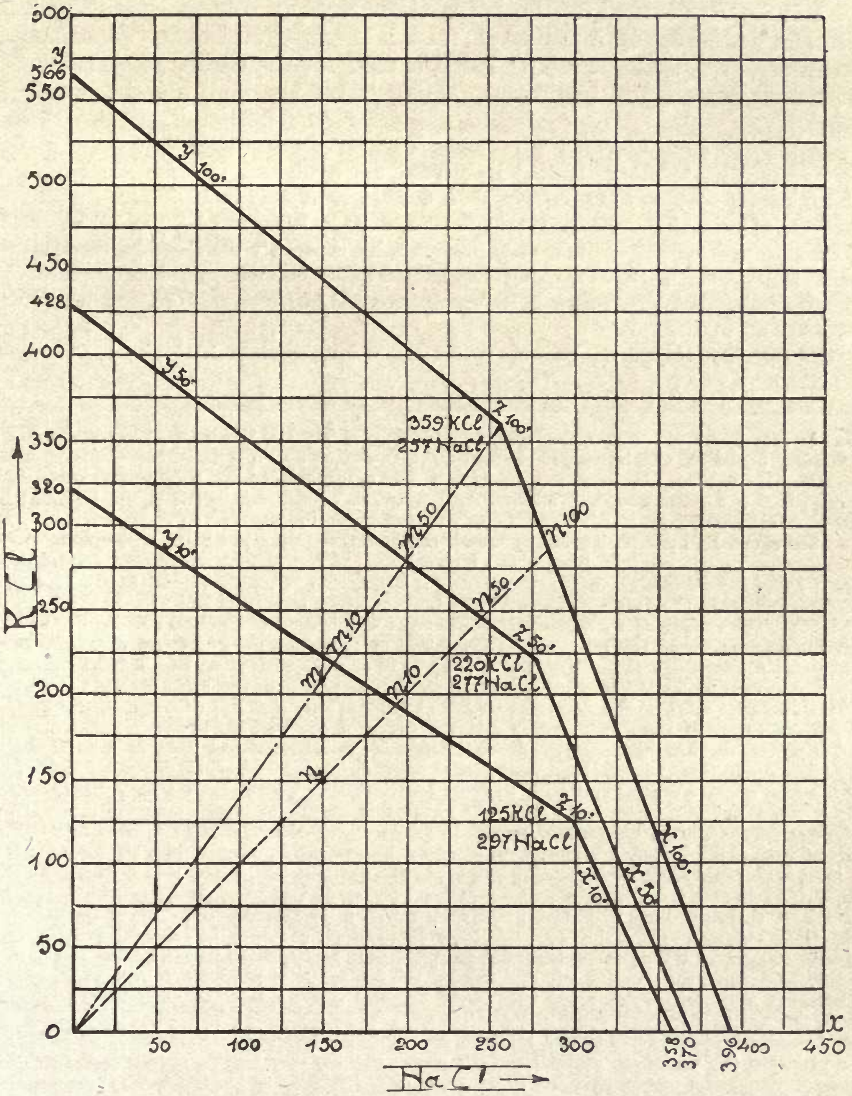


FIG. 209.

---

[1] Good crude Stassfurt carnallite contains about 23 per cent. of NaCl, 15 per cent. of kieserite ($MgSO_4$, H_2O), 2 per cent. $CaSO_4$, and 60 per cent. of true carnallite, the actual percentage of KCl being about 16. Systematic lixiviation and agitation with water dissolves and removes the magnesium chloride and a great part of the magnesium sulphate, but the residual undissolved potassium chloride still contains sensible amounts of NaCl, which are removable with difficulty, since at 20° NaCl and KCl dissolve almost equally in water, whereas in hot water the KCl is much more soluble than in the cold, but the NaCl only slightly more soluble (*see* diagram, p. 541). Taking into account the solubilities of the separate salts and those of different mixtures of the two salts at 10°, 50° and 100°, as shown in the diagram (Fig. 209), it is possible to fix exactly the conditions necessary for separating pure potassium chloride.

On the axis of ordinates *oy* are shown the solubilities of potassium chloride (at 10°, 320 grms, In order to avoid the accumulation of the mother-liquors of $MgCl_2$, A. Cappel (Ger. Pat. 259,112 of 1912) suggests a special treatment of carnallite in the dry in a furnace at 300° to 400° in presence of steam, all the chlorine of the $MgCl_2$ being thus evolved as HCl, which is condensed; when the remaining mass is treated with water (while a current of flue gases rich in CO_2 is passed to convert MgO into insoluble $MgCO_3$), only KCl is dissolved.

USES. KCl is used for the preparation of many other salts (*e. g.*, chlorate, perchlorate, etc.), and in the crude form it is employed in large quantities as a fertiliser (*see* pp. 531, *et seq.*). Much is used for the electrolytic manufacture of caustic potash, and immense quantities are converted into the nitrate (*see later*).

STATISTICS AND PRICES. Italy produced 5,000 tons of crude chloride in 1905 and imported 3460 tons (£33,200) in 1904, 4036 in 1906, 5812 in 1908, 8154 in 1910, 7327 in 1911, 8153 in 1912, 7060 (£60,720) in 1913, 6290 in 1914, and 1710 in 1915.[1] In 1905 Germany exported 157,100 tons of potassium salts, especially the chloride, the total value being £1,106,000; in 1909 the exports amounted to 220,000 tons out of an output of about 300,000 tons. The production in Germany was 511,260 tons in 1908 and 629,400 tons (£3,280,000) in 1909.

In 1910 the United States imported 190,000 tons, and in 1911 about 250,000 tons (£1,520,000).

KCl in 1000 grms. of water, at 50° 428, and at 100° 566 grms.), and on the axis of abscissæ the solubility of sodium chloride (at 10° 358, at 50° 370, and at 100° 396 grms. NaCl in 1000 grms. of water). If solid NaCl is added to a solution of KCl saturated at 100°, NaCl passes into solution, whilst KCl is precipitated, and on continual agitation equilibrium between the KCl and NaCl dissolved to saturation is reached. Such solution saturated at 100° contains 257 grms. NaCl and 359 grms. KCl per 1000 grms. of water, corresponding with the point *z* 100, *i. e.*, with the intersection of the straight lines *y* 100 and *x* 100. At 50° the corresponding concentrations are 277 and 220 for NaCl and KCl respectively (*z* 50), and at 10°, 297 and 125 (*z* 10). Along the line *yz* are marked the limits of saturation for KCl and along the line *xz* those for NaCl (in presence of KCl). The surface *o y z x* comprises all the possible solutions of NaCl and KCl. For instance, a solution containing 150 grms. of KCl and 150 of NaCl per 1000 of water corresponds with the point *n*, and one with 200 grms. of KCl and 150 of NaCl with point *m*. These two solutions are not saturated, and if they are concentrated by evaporation, the ratio between the weights of the two salts remains constant, since only the water is expelled, but when for the first solution a concentration of 190 grms. of KCl and 190 grms. of NaCl at 10° is reached the saturation point *n* 10 is reached, while for the second, 235 grms. of KCl and 160 grms. of NaCl correspond with the saturation point *m* 10. With either solution further concentration at 10° leads to the separation of pure crystallised KCl, the solution becoming weaker in KCl and correspondingly stronger in NaCl, in accordance with the saturation points marked along the line *n* 10 *z* 0. Further concentration, but at 100°, results in displacement of *n* to *n* 100 and of *m* to *z* 100, and whilst with *n* 100 further concentration leads to the separation of only pure sodium chloride in amounts corresponding with those shown along the straight line, *n* 100 *x* 100, with *z* 100 NaCl and KCl separate simultaneously in quantities such as do not displace the ratio between NaCl and KCl corresponding with the point *z* 100. If, however, this solution is cooled to 50°, only KCl separates, since the KCl line is again reached, the amount separating being 359 — 220 = 139 grms.; if the cooling is carried to 10°, the amount separating will be 359 — 125 = 234 grms. KCl, while the solution will still contain the 257 grms. of NaCl which were there at *z* 100, so that it is no longer saturated with NaCl, since at *z* 100 saturation with NaCl corresponds with 297 grms.

Hence, to separate KCl from a mixture of KCl and NaCl, solutions saturated at 100° should be prepared (by prolonged agitation of the mass until the composition corresponds with *z* 100, the solution being passed over fresh quantities of the original saline mixture), these depositing only KCl when simply cooled to 10°. The residual mother-liquors will contain 125 grms. of KCl and 257 grms. of NaCl and may be used again (after being heated to 100°) to treat a fresh quantity of the original salt, from which it extracts almost exclusively potassium chloride, this being separated by cooling to 10°, and so on. Thus, to extract only KCl from a mixture of it with NaCl, a solution of 257 grms. of NaCl in 1000 of water should be used. Naturally the salt remaining undissolved becomes poorer in KCl and richer in NaCl and longer agitation and contact are necessary to give almost complete separation.

[1] A parcel of Ethiopian potassium chloride (*see* p. 533) which arrived in Italy in 1917 had the composition: 3·37 per cent. of matter insoluble in water, 0·91 per cent. moisture (at 170°), and the following soluble components: 89·01 per cent. KCl, 4·54 per cent. NaCl, 1·52 per cent. P_2O_5, 0·12 per cent. SO_2, 0·03 per cent. $Fe_2O_3 + Al_2O_3$, 0·03 per cent. SiO_2, 0·04 per cent. MgO, 0·05 per cent. CaO, and 0·03 per cent. NH_3. The different qualities are, however, not very carefully separated, so that some deliveries contain only 60 to 65 per cent. KCl.

The commercial product with 80 to 90 per cent. KCl costs at Genoa about £10 per ton, and the chemically pure salt £70.[1]

POTASSIUM BROMIDE: KBr. This compound is obtained by treating a hot solution of potassium hydroxide with bromine : $6KOH + 3Br_2 = 5BrK + 3H_2O + BrO_3K$. The solution is evaporated to dryness, mixed with carbon, and then heated to redness; all the bromate is thus transformed into potassium bromide : $BrO_3K + 3C = 3CO + BrK$. It is more commonly prepared from a solution of ferroso-ferric bromide, Fe_3Br_8, by heating it with a solution of potassium carbonate. The precipitated iron, consisting of carbonate, oxide, etc., is separated by a filter-press, and the solution is then concentrated. The solution is purified by recrystallisation from water.

This bromide is a white salt of sp. gr. 2·4, easily soluble in water, but less soluble in alcohol; it melts at 740°, has a very salty taste, and is used in photography, and in medicine as a sedative. It costs 4*s.* per kilo retail, or £8 per 100 kilos in large quantities.

In 1905 Germany exported 634 tons of KBr and other bromides of the value of £69,760. In 1907 Italy imported 19·8 tons of the bromide, in 1909 32·7 tons, of the value of £2616, and in 1910 16·6 tons.

POTASSIUM IODIDE : KI. This compound is obtained in the same manner as the bromide, but the potassium iodate produced may be reduced with hydrogen peroxide : $IO_3K + 3H_2O_2 = IK + 3H_2O + 3O_2$.

It is obtained pharmaceutically by first preparing a ferroso-ferric iodide, FeI_2, Fe_2I_6, by the interaction of iron on iodine, and then decomposing this with a hot solution of potassium carbonate : $Fe_3I_8 + 4K_2CO_3 = 8KI + 4CO_2 + Fe_3O_4$.

Considerable quantities are to-day prepared from the cuprous iodide obtained in the treatment of Chili saltpetre, the copper being separated with H_2S.

It forms white cubical crystals of sp. gr. 3; it melts at 720° and then easily evaporates. 10 parts of KI dissolve in 7 parts of water or 25 parts of alcohol. Various metallic iodides which are insoluble in water dissolve in aqueous solutions of KI, forming double salts, such as HgI_2, 2KI.

Solutions of KI dissolve also considerable quantities of iodine, as an I_3 ion (from KI_3) is formed in solution, which is only partially dissociated into I_2 and I.

KI is much used in medicine because it accelerates the metabolism of the blood and is of use after mercurial treatment. It is also employed in photography. It costs about £1 per kilo.

In 1905 Germany alone exported 170·4 tons of KI and other iodine preparations, valued at £263,960. In 1904 Italy imported 37·9 tons of bromides and iodides at an average price of 5*s.* 7*d.* per kilo, in 1906 it imported 53·5 tons of iodides, in 1908 20·6 tons, valued at £18,128, in 1910 25·5 tons, and in 1911 23·2 tons.

POTASSIUM FLUORIDE : KF. This compound is obtained by neutralising hydrofluoric acid with potassium carbonate. It is a salt which dissolves in water and attacks glass. It easily forms double salts with other salts of less electropositive metals, and with HF it forms potassium hydrogen fluoride, KF, 2HF and also KF, 3HF.

With hydrofluosilicic acid, SiF_6H_2, solutions of potassium salts form a gelatinous precipitate of *potassium fluosilicate*, SiF_6K_2, which is only very slightly soluble in water.

POTASSIUM HYPOCHLORITE : ClOK. This compound is obtained from KOH and Cl, but if excess of chlorine is present, potassium chlorate is formed, especially on heating :

$$2KOH + Cl_2 = KCl + ClOK + H_2O.$$

It is known only in aqueous solution and was formerly much used for bleaching vegetable fibres under the name of "eau de Javelle"; for this purpose, sodium hypochlorite is now preferably used (*see below*). On evaporating this solution to dryness it decomposes :

$$3ClOK = 2KCl + ClO_3K.$$

---

[1] Potassium salts are sold on the basis either of the percentage of pure salt or of the percentaeg of the oxide (K_2O); 1 part of KCl corresponds with 0·6314 part of K_2O and 1 part of K_2SO, with 0·5407 part of K_2O.

POTASSIUM CHLORATE : $KClO_3$

Whilst the hypochlorite is formed with a limited quantity of chlorine, the chlorate is obtained by passing excess of chlorine into a solution of potassium hydroxide, even in the cold, but better at 90° :

$$6KOH + 3Cl_2 = 5KCl + 3H_2O + KClO_3;$$

it is obtained also by heating the solution of the hypochlorite :

$$3ClOK = KClO_3 + 2KCl.$$

Until a few years ago the chlorate was prepared on the large scale by the old process of Liebig (1842) by passing chlorine into milk of lime, contained in cast-iron cylinders provided with stirrers, at 40°. A solution of calcium chlorate was thus obtained, and after filtration was decomposed with the calculated quantity of potassium chloride. The liquid was partially evaporated, and crystals of potassium chlorate, which is not very soluble, were then obtained and were purified by recrystallisation from water :

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2ClO_3K.$$

In this process some chlorine is lost in the form of $CaCl_2$, which is of no value. To-day it has been replaced by the electrolytic method, since Oettel has shown that on electrolysing concentrated alkaline solutions of potassium chloride in the hot, potassium chlorate is readily obtained. The process of Galle and Montlaur, who used diaphragms, was first employed, but to-day diaphragms are largely dispensed with. Lederlin improved the yield by keeping the bath feebly acid, *e. g.*, by eliminating a little of the cathode product—as suggested by Silbermann (Ger. Pat. 205,019).

The electrolysis is conducted in lead-lined wooden vessels of a capacity of 5 cu. metres, which are insulated below by a vessel of oil. The anodes are formed of iridio-platinum plates containing 10 per cent. of iridium, 1 mm. thick. The cathodes are formed of an alloy of iron and nickel coated with asbestos in order to discharge the hydrogen the more readily. On working with a current of 465 amps. at an E.M.F. of 5 volts, the temperature of the electrolyte is raised to 45°, and then the transformation of the hypochlorite, which is first formed, into potassium chlorate occurs. This crystallises and separates, whilst the bath is gradually replenished with more potassium chloride. One horse-power is consumed per 24 hours in order to obtain 1 kilo of potassium chlorate.

C. Kellner electrolyses a solution of potassium chloride, saturated in the cold, without diaphragms with the addition of about 3 per cent. of potassium hydroxide, which is not all dissolved, and suspends in the solution a little calcium hydroxide, which absorbs the small amount of chlorine remaining free at the anode.

The electrolytic manufacture of chlorates was started in 1891 in Switzerland. It then spread to England, France, and Germany in 1894, but the industry can be profitably developed only in countries where large water powers are available at a cheap rate. These works are to-day found specially in Switzerland, France, Finland, Sweden, Norway, and Italy. The largest chlorate works is at Chedde (Switzerland) and has been in operation since 1896, the Corbin and Lederlin process being in use.

In the Italian works at Legnano the electrolysis is carried out in large stoneware vessels of about 1000 litres capacity with a 25 per cent. solution of potassium chloride, containing 1 per cent. of pure potassium dichromate and previously freed from sulphates or sulphuric acid by means of $BaCl_2$; current at 3·5 to 4 volts is used and in about two hours the temperature rises to 65° to 70°, when the current is suddenly cut off, so that the chlorate—coloured yellow by the dichromate and by a little iron, which are mostly eliminated by centrifugation—may separate on cooling. The mother-liquors are strengthened with more potassium chloride and a little dichromate and are then pumped back into the electrolytic baths. The method used for purifying the chlorate consists in dissolving it in hot water, adding a little $BaCl_2$ to precipitate the chromium and filtering to remove this and also the iron. From the hot solution the crystallised chlorate is separated by cooling, this process being repeated; the mother-liquors are removed by decantation and draining, rather than by centrifugation.

The resulting product is very white and of a purity of 98 to 99 per cent. With 700 kw.-hours, 100 kilos of potassium chlorate are produced from 61 kilos of chloride. Special electrodes are used which are more resistant and economical than those of Acheson graphite. In the works at Bussi sodium chlorate is formed as a secondary product in the manufacture of electrolytic sodium hydroxide. According to Ger. Pat. 235,706 and Fr. Pat. 421,618, the dichromate may be replaced with advantage by cerium chloride.

In Germany chlorate is obtained by direct electrolysis of carnallite, but it then contains as much as 0·25 per cent. of $KBrO_3$, whereas that used for explosive purposes should contain less than 0·15 per cent. of bromates.

Potassium chlorate crystallises in monoclinic plates and is only slightly soluble in cold water (5 per cent.). It produces a cooling and slightly sharp effect on the palate. It melts at 300°, and when the temperature is further raised, immediately evolves oxygen, forming KCl and potassium perchlorate, $KClO_4$, which yields O and KCl at still higher temperatures.

With HCl, $KClO_3$ evolves chlorine:

$$KClO_3 + 6HCl = KCl + 3Cl_2 + 3H_2O.$$

It is an oxidising agent, and when mixed carefully with red phosphorus, very slight friction is sufficient to cause the mixture to detonate violently. Also, on mixing potassium chlorate cautiously with antimony sulphide by means of a feather a mixture is obtained which easily explodes by friction or shock.

During the transformation of the chlorate into chloride and oxygen—which occurs by heating up to the melting-point—33·4 Kj. (7960 cals.) are evolved.

Potassium chlorate is employed in match factories, especially for Swedish matches, and also in firework factories, for percussion caps and in certain explosive powders. It is likewise used in dyeing, for oxidising various substances which produce aniline black, and this oxidising action, which does not occur at ordinary temperatures, is accelerated by the addition of minimal quantities of catalytic substances, such as copper and vanadium salts. To-day, however, potassium chlorate has been partially replaced by sodium chlorate, which costs less and produces the same effects as the potassium salt.

Crystallised potassium chlorate cost £34 per ton before the war, whilst before electrolytic processes were introduced it cost £60. The chemically pure product costs £40 per ton.

In 1887 the world's production of potassium chlorate was 6750 tons, of which 5500 were produced in England, and in 1900 it was 17,500 tons, one-third of this amount being made electrolytically. The position is completely changed to-day, and the "Société d'Electrochimie" alone produces annually 1800 tons at St. Michel and at Vallorbe in Switzerland, by the use of 3000 h.p. at £8 per h.p.-year.

In Europe 7 works were in operation in 1900, using 28,000 h.p. altogether, and with a total production of 9000 tons of chlorate. In 1907 the two factories at St. Michel and Chedde produced together 7000 tons of chlorate. In Italy there is a sodium chlorate works at Bussi, belonging to the "Società elettrochimica of Rome," which produced 217 tons, in 1908, of the value of £7024, and a potassium chlorate works at Legnano ("Società elettrochimica Rossi"), which was in full work in 1909, and is capable of turning out 350 tons per annum. In 1914 the Italian output was 570 tons and in 1915 700 tons. Italy imported 195 tons of chlorates and perchlorates of sodium and potassium in 1906, about 652 tons in 1907, about 365 tons in 1908, of the value of £11,658, and 144 tons in 1914. The protective tariff in Italy is £8 per ton, and moreover all the European works are members of a syndicate.

In 1905 Germany imported 2054·2 tons of chlorate, of the value of £54,400, and exported 1069·9 tons, of the value of £29,400, that is, at £27 10*s*. per ton. In 1909 it imported 1300 tons and exported 1200 tons. France exported 631 tons in 1910, 427 in 1911, 1087 (and

945 of sodium and barium chlorates) in 1913, 962 (and 9448 of sodium and barium chlorates) in 1915, and 2227 (and 23,794 of sodium and barium chlorates) in 1916.

POTASSIUM PERCHLORATE: $KClO_4$, is obtained mixed with KCl when potassium chlorate is heated till fused, after the first phase of the evolution of oxygen: $2KClO_3 = KClO_4 + KCl + O_2$; the perchlorate may then be separated from the chloride, because the latter is much more soluble in water. The electrolytic preparation is similar to that of sodium perchlorate. It starts from sodium chloride, which is first converted into the chlorate, and this again subjected to electrolysis in a concentrated cold solution, the mass being cooled with water in coils. The dissolved sodium perchlorate is then treated with a concentrated solution of potassium chloride, when crystalline potassium perchlorate separates, being less soluble than sodium perchlorate: $NaClO_4 + KCl = KClO_4 + NaCl$. Apparently the presence of a little dichromate increases the yield (Ger. Pat. 136,678).

Its oxygen is not as active as that of the chlorate, and its oxidising power is only exerted in the undissolved condition at high temperatures.

It is used industrially for fireworks, instead of a portion of the chlorate, because it is more stable, and is also used in the explosive industry on account of the large amount of oxygen which it contains.

The crude perchlorate costs £20 per ton; when refined it costs £48 per ton.

POTASSIUM BROMATE and **IODATE** are similar to the chlorate.

A compound, KHI_2O_6, **Acid Potassium Iodate**, and also **Potassium Periodate**, KIO_4, are known; so are the potassium salts corresponding with the following hydroxides: $I(OH)_7$, $IO(OH)_5$, etc.

POTASSIUM NITRATE: KNO_3 (NITRE, SALTPETRE)

This compound is one of those salts which have been known and used since ancient times. It is found abundantly in the East Indies, in Bengal and Bombay, and in the caves of Ceylon, which were once inhabited by animals and by men, but are to-day tenanted only by bats; it is found as an efflorescence in many soils and especially in hot countries, such as Peru, Bolivia, South Africa, and Egypt. At the beginning of last century it was obtained by making mounds of earth, potassium salts (such as plant ashes) and decomposing nitrogenous organic matter (such as stable manure), the mounds being afterwards moistened from time to time; the whole is then abandoned to the action of nitrifying bacteria for a year or more. Calcium nitrate is first formed with the lime always present in the soil, this then giving potassium nitrate in contact with the potassium carbonate; the nitrate is finally extracted with water:

$$(NO_3)_2Ca + CO_3K_2 = 2NO_3K + CO_3Ca.$$

The saltpetre which abounds in the soil of British India and especially in that of Ceylon has been produced in this way. Considerable quantities of this saltpetre have even been extracted to supply Europe for the manufacture of explosives, for which purpose it is preferred, owing to the absence of perchlorates.[1] In the Middle Ages it was scraped from the walls of cellars, where it is found as an efflorescence owing to the infiltration of terrestrial waters, in which it is continually formed. After 1855 (the Crimean War)

---

[1] In certain parts of India the soil contains as much as 29 per cent. of potassium nitrate, and 3 to 5 per cent. is common. It is extracted by lixiviating the soil with water and either allowing the solution to evaporate by the sun's heat in large basins or heating it with wood in large boilers. The crusts which separate at the surface of the liquid are removed, these consisting of potassium and magnesium nitrates, sodium and potassium chlorides and sodium sulphate. The crusts are treated with hot saturated solutions of sodium chloride and sulphate, which dissolve only the potassium nitrate, this separating almost pure on cooling and being sold to the English refiners; the mother-liquors are used for lixiviating fresh soil.

The crude nitre is refined by heating it to boiling with the mother-liquors from preceding operations in an open vessel with a stirrer, the solution being forced through a heated double filter by means of compressed gas. The hot saturated filtrate is cooled in vessels furnished with stirrers, so that the nitre separates rapidly in fine crystals; the whole mass is then centrifuged and the mother-liquors used again, while the nitre—of 90 per cent. strength—is washed on the moving centrifuge with one-tenth of its weight of water, the strength being thus increased to 94 per cent. The impurities left on the filter are lixiviated with fresh water.

potassium nitrate for gunpowder became a product which was largely consumed, and the so-called *conversion nitrate* was then prepared in Germany by evaporating a saturated solution of sodium nitrate (Chili saltpetre) with potassium chloride (from Stassfurt) in molecular proportions. When the solution acquires a density of 1·5 almost all the excess of sodium chloride, which is less soluble on heating, separates, and when the solution has cleared (helped by the addition of a little glue) and after repeated decantation of the clear hot liquid, it is allowed to crystallise in vats with stirrers in order to obtain the potassium nitrate as a crystalline powder. The separation on cooling is copious and almost complete, because potassium nitrate is very slightly soluble in cold water, though very soluble in hot (*see* Fig. 210), whilst the residual sodium chloride remains in solution, as its solubility in the cold and on heating is almost the same:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The crystalline mass is then separated from the mother-liquors by decantation and passed into a hydro-extractor, the cage of which is made of fine metallic netting, and is there washed with a gentle spray of cold water whilst the hydro-extractor is in motion.[1]

The product is then completely dried in copper pans in a current of hot air. If the nitrate is to be used for the manufacture of black gunpowder, it should not contain more than 0·0003 per cent. of chlorides, which are deliquescent.

The conversion of sodium into potassium nitrate is easily understood on considering the solubility of these salts. Four different ions are present in solution, $K^{\cdot}$, $Na^{\cdot}$, Cl', NO_3', and on concentration those ions which form the less soluble salt, namely, NaCl, separate during cooling.

The diagram of solubilities (Fig. 210), shows the solubility of these four salts at various temperatures and expressed in molecular weights. We thus see that at 0° 5 mols. (that is, 290 grms.) of NaCl, 1·2 mols. of KNO_3, 3·5 mols. of KCl and 9 mols. of $NaNO_3$ dissolve in the same quantity of water. At 100° the ratio of the solubilities is completely changed. The solubility of NaCl is maintained at almost the same figure, that is, the curve representing NaCl in the diagram is almost horizontal; on the other hand, 15 mols. of potassium nitrate (that is, about 2500 grms), are dissolved at 100°, about 21 mols. of sodium nitrate and about 7 mols. of KCl, and the *solubility curves* vary greatly. Thus, on cooling the solution saturated at 100°, the KNO_3, which is very soluble in the hot and much less so in the cold, will separate, whilst

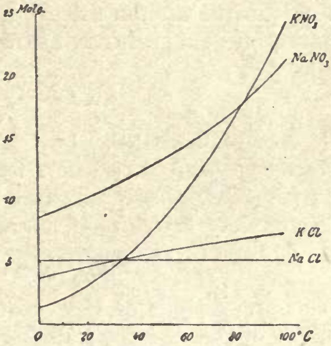


FIG. 210.

---

[1] The brown mother-liquors have the density 1·45 to 1·50 and contain a certain amount of iodine. Milbauer (1912) gives the following compositions (grams per litre) for two mother-liquors (*a*, *b*) from an Austro-Hungarian factory: Dry residue, 580·82 (*a*), 547·23 (0·6 insoluble) (*b*); NaCl, 317·2 (*a*), 259·32 (*b*); KCl, 16·74 (*a*), 51·73 (*b*); KNO_3, 138·3 (*a*), 105·57 (*b*); KI, 2·28 (*a*), 8·54 (*b*); KIO_3, 14·33 (*a*), 0·25 (*b*); $MgSO_4$, 10·02 (*a*), 6·42 (*b*); K_2SO_4, 80·06 (*a*), 7·76 (*b*); $CaSO_4$, 0·91 (*b*); aluminium sulphate, 3·70 (*b*); traces of bromine, potassium carbonate, organic matter and iodoform in both; reaction faintly alkaline. When evaporated further, these mother-liquors deposit salt, but part of the iodine is vaporised and lost at the same time. To avoid such loss, the concentration is carried out in presence of sodium sulphite (rather more than 1 grm.-mol. per grm.-mol. of iodine present), the salt being filtered off and the solution acidified with sulphuric acid and the iodine precipitated, by addition of copper sulphate (2 grm.-mols. per grm.-mol. of iodine) and soda, in the form of Cu_2I_2. The latter is collected on a filter (if it is very fine, the first portions of the filtrate are returned to the filter) and washed with water, the 5 to 8 per cent. of chlorides it still retains being converted into iodides by heating the moist mass of Cu_2I_2 with water and a little KI ($Cu_2Cl_2 + 2KI = Cu_2I_2 + 2KCl$). The pure Cu_2I_2 is filtered off and converted into KI by boiling it with K_2CO_3, the solution being decanted off from the precipitated red Cu_2O, and a little hydrogen sulphide then passed through it to precipitate traces of copper still dissolved. The liquid is then filtered and evaporated until pure potassium iodide crystallises out, the mother-liquors being put into circulation again for treating new portions of copper iodide.

the NaCl, which changes its solubility very little with change of temperature, will remain in solution.

In a *saturated* aqueous solution of a given salt, a certain quantity of another salt, which has no ions corresponding with those of the first salt, may be dissolved. On the other hand, a second salt, one of the ions of which is the same as one of those of the first salt, if added in minimal quantity immediately causes supersaturation and ready separation of the first salt. Thus, sodium chloride or magnesium sulphate may be added to a saturated solution of potassium perchlorate without separation of the perchlorate, but if a minimal quantity of potassium chloride, which has the same $K^{\cdot}$ cation as the perchlorate, or of sodium perchlorate, which has the same ClO_4' anion, is added, potassium perchlorate separates immediately, being the less soluble salt. In general, therefore, a salt solution may also be saturated by the concentration of one only of the ions of the salt itself, thus causing the separation of the ions of the less soluble salt. This rule may be employed for the separation of various salts from solutions of their mixtures, for example, to eliminate gypsum from strong solutions of sodium chloride, as this accumulates in such quantities in the vacuum pans that it produces thick incrustations which render concentration more difficult (*see below*).

KNO_3 crystallises in hexagonal rhombic prisms without water of crystallisation. 100 parts of water dissolve 247 parts of the nitrate at 100° and only 13 parts at 0°.

It has a sharp taste, melts at 339°, and decomposes at a higher temperature into potassium nitrite, KNO_2, and oxygen. When heated to redness with carbon it deflagrates and forms potassium carbonate, with evolution of nitrogen and CO_2:

$$4KNO_3 + 5C = 3CO_2 + 2N_2 + 2K_2CO_3.$$

APPLICATIONS. Potassium nitrate is used in the manufacture of *common black gunpowder*, which contains 75 per cent. of potassium nitrate, 12 per cent. of sulphur, and 13 per cent. of wood charcoal. On ignition there is complete interaction, mainly according to the following equation:

$$2KNO_3 + S + 2C = K_2SO_4 + N_2 + 2CO.$$

The proportions of the constituents vary, however, somewhat in the various types of powder (for cannons, fuses, mines, etc.), but all the oxygen for the combustion of the carbon and sulphur is furnished by the nitrate.

The power of gunpowder is due to the abundant formation of various gases, especially N, CO, and CO_2, which occupy a volume 1000 times larger than the solid powder. The potassium nitrate is now largely replaced by ammonium nitrate, which burns without leaving any residue. Potassium nitrate is also used for the preservation of meat (pickled beef, etc.), and as a rapidly acting manure.

In 1913 refined potassium nitrate cost about £22 per ton, and when chemically pure up to £34.

1200 tons were produced in Italy in 1904, 2000 tons in 1907, 1900 tons in 1908, of the value of £41,800, 950 tons in 1914, and 538 tons (£25,588) in 1915; 376 tons (£7800) were imported in 1904, 228 in 1906, 580 in 1907, 381 in 1908, 984 in 1910, and 344 (£7700) in 1911.

In 1905 Germany exported 10,460 tons (£225,000) of potassium nitrate, and in 1909 exported 12,475 tons and imported 2853 tons.

The United States imported 5750 tons in 1910 and 3750 tons (£53,000) in 1911.

Great Britain imported 10,500 tons in 1909, 11,400 tons (£21,640) in 1910, and 11,200 tons in 1911. India produced 20,000 tons in 1880, 19,900 in 1903, 17,900 in 1907, 18,500 in 1908, and 20,000 in 1911.

POTASSIUM NITRITE: KNO_2

This compound is obtained in the same manner as sodium nitrite, for instance, by reducing 1 part of potassium nitrate with 2 parts of lead (or with Fe or Cu); lead oxide is formed which is insoluble in water, whilst the nitrite dissolves and may then be separated and crystallised. Nowadays it is also prepared industrially from a mixture of CaO and a concentrated solution of potassium nitrate, into which sulphur dioxide, free from air, is passed in the hot: $KNO_3 + CaO + SO_2 = SO_4Ca + KNO_2$. The yield is excellent and the insoluble calcium sulphate is easily separated. A good yield is also obtained by melting together KNO_3 and KOH and reducing at about 350° with a sulphite.

It forms white crystals which melt easily and deliquesce in the air, as they are very soluble in water. On the other hand, they are insoluble in alcohol. It is used in the preparation of organic azo-compounds and costs £76 per ton. When chemically pure in sticks, it costs 4*s.* per kilo.

POTASSIUM SULPHATE: K_2SO_4

This compound is obtained from KCl with sulphuric acid and from solutions of *kainit* (K_2SO_4, $SO_4Mg + MgCl_2 + 6H_2O$) at Stassfurt (the true composition of kainit is given on p. 530). On concentrating solutions of this substance, magnesium and potassium sulphates separate in the form of *schönite*, K_2SO_4, $MgSO_4$, $6H_2O$, which forms potassium sulphate and $MgCl_2$ on concentration with excess of potassium chloride; *kieserite*, $MgSO_4$, H_2O, acts in the same way:

$$K_2SO_4,\ MgSO_4 + 2KCl = 2K_2SO_4 + MgCl_2.$$

Potassium sulphate, being less soluble than magnesium chloride, is easily separated on concentrating the solution.

According to Ger. Pat. 270,620 (1912) the whole of the potassium sulphate remaining in the mother-liquors of schönite and kainit may be recovered by treatment with an amount of calcium chloride solution depending on their content of magnesium salts: K_2SO_4, $MgSO_4 + CaCl_2 + H_2O = K_2SO_4$, $CaSO_4$, $H_2O + MgCl_2$. After agitation for 15 minutes, the double calcium and potassium sulphate separates in a crystalline form; it is collected on a filter, washed and calcined, and may then be used as a fertiliser or to mix with highly concentrated potassium sulphate. The filtrate is free from sulphates and is treated like other liquors containing magnesium chloride.

It forms small rhombic prisms without water of crystallisation and has a slightly bitter taste; at 15° it is dissolved by water to the extent of 19 per cent.; it melts at 1070°.

It is used as a potash fertiliser, and in alum and glass works, and also in works producing potassium carbonate by the Leblanc process. In Germany the use, as a fertiliser, of the calcined sulphate of magnesium and potassium is preferred, being more economical.

Italy imported 1566 tons of potassium sulphate in 1902, 1663 tons in 1904, 3866 tons in 1907, 4910 tons (£56,736) in 1908, 7753 tons in 1910, 13,466 tons in 1912, 9454 tons in 1913, 3708 tons in 1914, and 900 tons in 1915. In 1905 Germany exported 6745·5 tons, worth about £440,000, and produced 47,994 tons, not including other sulphates, such as kainit, etc.; in 1909 Germany exported 63,107 tons of potassium sulphate. The United States imported 43,000 tons in 1910 and 60,000 in 1911.

For potash fertiliser it is sold in Italy at about £11 per ton, while the puriss. salt costs £30.

POTASSIUM HYDROGEN SULPHATE, POTASSIUM BISULPHATE: $KHSO_4$. This compound is obtained from the neutral sulphate with H_2SO_4 or directly from KCl and H_2SO_4 at a moderate heat. It forms rhombic tablets very soluble in water. It melts at 200°, with loss of water, and is then transformed into potassium pyrosulphate, $K_2S_2O_7$, which forms SO_3 and K_2SO_4 at 600°.

It shows an acid reaction because its anion, HSO_4', is partially decomposed in aqueous solution into $H^{\cdot}$ and SO_4''. It is used to some extent in making cream of tartar, but for this purpose must be free from lead.

POTASSIUM PERSULPHATE: $K_2S_2O_8$. This is obtained in crystals at the positive pole (anode) in the electrolysis of a concentrated solution of $KHSO_4$, hydrogen being evolved at the cathode: $2KHSO_4 = H_2 + K_2S_2O_8$ (*see* p. 328).

Its aqueous solution has a very saline taste. It is an oxidising agent and the solid salt evolves oxygen even at 100°, forming potassium pyrosulphate.

POTASSIUM SULPHITE and BISULPHITE: $K_2SO_3, 2H_2O$ and $KHSO_3$, are obtained by passing SO_2 through a hot solution of K_2CO_3, until no more CO_2 is evolved (*see below;* Sodium Sulphite). When heated, potassium bisulphite loses a molecule of water and forms **Potassium Pyrosulphite,** $K_2S_2O_5$, sometimes improperly termed **Potassium Metabisulphite,** which is manufactured on a large scale by passing SO_2 into a hot, saturated solution of potassium carbonate until effervescence ceases and the liquid assumes a greenish colour; on cooling, the liquid deposits white crystals (monoclinic prisms) of metabisulphite, which is sparingly soluble in cold water and if heated strongly in the air decomposes into $K_2SO_4 + SO_2 + S$. The sulphite is more soluble in the cold than in the hot.

For twenty years large amounts of the metabisulphite have been used in the wine industry in Italy.[1]

POTASSIUM SULPHIDE: K_2S. This compound is prepared by heating a mixture of potassium sulphate and carbon in well-closed crucibles to a moderate temperature:

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

The fused mass then forms a red, crystalline substance soluble in water. On concentrating the aqueous solution, $K_2S, 5H_2O$ crystallises in colourless prisms which are deliquescent in the air. The solution readily absorbs oxygen from the air with formation of **Potassium Thiosulphate:**

$$2K_2S + H_2O + 2O_2 = 2KOH + K_2S_2O_3.$$

Many solutions of metallic salts separate insoluble metallic sulphides on treatment with K_2S. It evolves H_2S with acids. It has a strongly alkaline reaction in aqueous solution because it is not dissociated into the ions $2K^{\cdot}$ and S'', as the latter combines with water forming SH' and OH', the OH' ions giving the alkaline reaction. In 1905 Germany imported 6573 tons of potassium and sodium sulphides of the value of £46,754. For the Italian imports and production, *see* Sodium Sulphide.

POTASSIUM HYDROSULPHIDE: KSH. This compound is obtained in aqueous solution by passing a current of H_2S into a solution of potassium hydroxide until this is saturated: $KOH + H_2S = H_2O + KSH$. On concentrating the liquid *in vacuo,* the hydrosulphide separates as crystals containing $2H_2O$, forming colourless rhombohedra which lose water at 200°; at higher temperatures it melts and then forms a red mass on cooling.

It shows an alkaline reaction and forms potassium sulphide with an equimolecular quantity of KOH: $KOH + KSH = H_2O + K_2S$.

POTASSIUM POLYSULPHIDES: K_2S_3, K_2S_4, K_2S_5. These compounds are easily formed with liberation of sulphur by boiling a solution of K_2S.

LIVER OF SULPHUR, which is employed medicinally, is obtained as a greenish-yellow mass by melting 2 parts of potassium carbonate with 1 part of sulphur, and consists of a mixture of K_2S_3, K_2SO_4, and $K_2S_2O_3$.

Certain metallic sulphides are soluble in potassium or sodium sulphide with formation of sulpho-salts (double sulphides).

---

[1] It serves to render more stable and more healthy wines with feeble tartaric acidity and to prevent secondary fermentation in virtue of the slow and continued evolution of SO_2. In general it is dissolved in a little water or must and added to the bulk of the must freshly expressed from the grape, but some add it to the grapes during pressing, and some to the wine itself. From 10 to 20 grms. per hectolitre are used, and it must be dissolved in wooden vessels, since metal ones are attacked and iron imparts a black colour to the wine after the evolution of SO_2 ceases, the whitish ferrous tannin compound then undergoing oxidation to the black ferric compound. Pure metabisulphite gives 53 per cent. of SO_2, and in the wine industry the potassium and not the sodium salt is used, since the former is easily obtainable in pure crystals, which are free from iron and remain unchanged in the air. On the other hand, the sodium salt crystallises with difficulty, absorbs moisture from the air, and with the tartaric acid of the wine forms sodium tartrate, which remains dissolved and increases the ash of the wine, whereas the potassium salt forms acid potassium tartrate (cream of tartar), which is only slightly soluble and separates easily from the wine.

POTASSIUM CARBONATE: K_2CO_3 (POTASH)

This compound is found in abundance in wood ashes and ashes of plants, these organisms containing potassium salts which are transformed into potassium carbonate at the expense of the organically combined carbon during combustion and incineration. The ashes, which contain from 10 to 20 per cent. of potassium salts, are lixiviated two or three times with water, and the clear solution, of 20° Bé., is concentrated in open iron pans and the residue calcined in furnaces; *crude potash* is thus obtained which is lixiviated and in turn forms purer potash, containing, however, a little soda, KCl, and K_2SO_4.

Very little vegetable ash is now used for the production of potash, except in Russia, with its immense forests, because it can be obtained more economically by other means.

Another abundant supply of potash has been known since 1840 in the residues of beet-sugar manufacture. The sugar-beets abstract from the soil very large quantities of potassium salts, which accumulate in the molasses from the sugar. These molasses, containing 45 to 50 per cent. of sugar and 3 to 4 per cent. of potash, are diluted with water and fermented in order to obtain alcohol, which is then distilled. The aqueous residue, of 4° Bé., which contains potassium salts, is concentrated in open pans or *in vacuo* up to 40° Bé.; the residue is then calcined in a furnace, or preferably in retorts in order to utilise the products of distillation which contain cyanogen compounds, NH_3, trimethylamine, etc. It is still better to pass these hot gases into red-hot furnaces, where ammonia and hydrocyanic acid are formed. The former is absorbed by passing the gases through concentrated sulphuric acid; the hydrocyanic acid is absorbed by solutions of sodium hydroxide. In this way a single works at Hildesheim in Germany produces 3·5 to 4 tons of sodium cyanide daily.

The solid carbonaceous residue from the calcination of the molasses contains 30 to 60 per cent. of K_2CO_3, which is extracted with water and the solution concentrated, K_2SO_4 and KCl being gradually removed as they crystallise out; when the concentration has reached 55° Bé., sodium carbonate also separates. The residue is dried in a furnace.

Rivière (1909) suggested the separation of potassium salts from molasses by means of aluminium and magnesium fluosilicates.

In Italy certain sugar refiners carbonise the molasses with hot furnace gases and then export the resulting crude potassium carbonate, almost entirely to Austria.

Considerable quantities of potassium carbonate may be obtained from the water which has been used for washing raw wool, as was already suggested in 1860. The raw Australian wool contains up to 50 per cent. of perspiration, and this substance is largely composed of fatty substances partially combined with potassium in the form of soaps, etc. The fat is first separated from the wool by extracting it with benzine, and on then evaporating the water in which the wool is washed and calcining the residue potassium carbonate remains, and is purified by redissolving it in water. This potassium carbonate contains less sodium salts than that from molasses.

It is also contained in the ashes of certain marine plants, which are treated in order to extract iodine and bromine.

Much potassium carbonate is prepared in Germany from the potassium chloride and sulphate of Stassfurt by the Leblanc process (*see below*, Soda). Lately, however, experiments have again been successfully undertaken on a vast scale, using the Engel-Precht process, which was patented in 1880 but had not then yielded satisfactory results. This process consists in mixing a solution of KCl with magnesium carbonate, then passing in a current of CO_2 and stirring the mass continuously; a double salt is first obtained:

$$3MgCO_3 + 2KCl + CO_2 + 9H_2O = 2(MgCO_3,\ CO_3KH,\ 4H_2O) + MgCl_2.$$

This is washed with a solution of magnesium bicarbonate in order to separate $MgCl_2$ without decomposing the double salt, the latter being then decomposed by water under pressure at 120°. Basic insoluble magnesium carbonate is precipitated, CO_2 is evolved, and the filtered solution of K_2CO_3 is evaporated and then calcined. By this means potassium carbonate free from sodium salts is obtained, as NaCl does not react with magnesium carbonate. Solvay has further improved this process (Ger. Pat. 159,870).

According to Ger. Pat. 266,786 of 1913, K_2CO_3 may be obtained by adding a powdered mixture of potassium sulphate and sodium carbonate to saturated sodium carbonate solution at 40° so as to have 2 mols of Na_2CO_3 per 3 mols. of K_2SO_4. The liquid is stirred for 3 to 4 hours and poured on to a suction filter, which retains the crystals of glaserite (double salt, K_2SO_4, Na_2SO_4) formed, whilst the potassium carbonate solution is concentrated as usual.

Chemically pure potassium carbonate is obtained by heating pure potassium tartrate or oxalate to redness, or, better still, by heating potassium bicarbonate.

PROPERTIES. Pure potassium carbonate forms a white granular powder which becomes deliquescent, 100 parts of water dissolving 83 parts at 0° and 205 parts at 135°. From concentrated solutions it sometimes crystallises with water of crystallisation, $2K_2CO_3 + H_2O$, and when hot, $K_2CO_3 + H_2O$; at 135° it remains anhydrous.

It melts at 890° and vaporises at a white heat. The aqueous solution has a strongly alkaline reaction because the CO_3'' anions in solution react with a part of the water itself: $CO_3'' + H_2O = CO_3H' + OH'$, and we thus have alkaline OH' anions (*see* Hydrolysis, p. 271).

Potassium carbonate has the property of being easily decomposed by acids with evolution of CO_2. In presence of soluble salts of the heavy metals it readily combines with these to form insoluble carbonates which separate, whilst a new soluble potassium salt, containing the acid residue which was combined with the heavy metal, remains in solution.

A table of densities of potassium carbonate solutions is given under the heading Sodium Carbonate.

Potassium carbonate is largely employed in the manufacture of soft soaps, and still larger quantities are used in making Bohemian glass, in dyeing, and in wool washing. When commercially pure it costs £24 per ton, and £38 when chemically pure,[1] whilst the crude product costs from £12 to £16.

The internal consumption in Germany in 1901 was 16,000 tons of potassium carbonate, and 15,000 tons were exported, of the value of about £280,000. In 1905 11,963 tons were exported and in 1907 about 13,300 tons, valued at £240,000. In 1910 15,000 tons of molasses potash were made, corresponding with 300,000 tons of molasses. Italy imported 913 tons of potassium carbonate in 1903; 604·2 in 1904; 838·4 in 1906; 825·3 in 1908, valued at £14,856, and 1237 in 1910. On the other hand, Italy exported the following quantities of crude potassium carbonate, produced in sugar factories, by calcining molasses: 56·8 tons in 1906; 483·7 tons in 1907; 741·3 tons in 1908; 2076 tons (£34,880) in 1910. In 1915 10 tons of potassium carbonate, valued at £196, were produced. Russia, which at one time exported potassium carbonate, now imports several thousand tons.

The United States imported 9400 tons of potassium carbonate in 1910 and 10,300 tons (£12,720) in 1911.

POTASSIUM BICARBONATE: $KHCO_3$ (Potassium hydrogen carbonate). This compound is obtained in crystals by passing carbon dioxide into a saturated solution of K_2CO_3; in a solution of the carbonate a large part of the CO_3'' ions are unaltered, and by means of a current of CO_2 in presence of water these are completely transformed into CO_3H' ions, thus: $CO_3'' + CO_2 + H_2O = 2CO_3H'$; on the other hand, there are also $K^{\cdot}$ cations in the solution and consequently all the carbonate is transformed into the bicarbonate, $CO_3K_2 + CO_2 + H_2O = 2CO_3HK$. The bicarbonate, being less soluble in water than the carbonate, readily separates in monoclinic crystals free from water. Water dissolves only about 20 to 25 per cent. of this substance, and solutions which are not very dilute

---

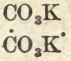
[1] Sometimes a solution of pure potash gives a faint reaction for chlorides, whilst if the carbonate is previously heated to redness, the aqueous solution gives the chloride reaction much more distinctly; this is due to the presence in the potash of a little potassium chlorate, which is derived from the electrolytic potash used in making the carbonate.

show a neutral reaction, whilst when very dilute they show a faint alkaline reaction, because a small part of the CO_3H' anions hydrolyse and form H_2CO_3 and OH' with water.

On simple evaporation the solution is decomposed into $CO_3K_2 + CO_2 + H_2O$, whilst the dry salt decomposes only at 110°.

The bicarbonate is used especially for the preparation of pure potassium carbonate, and costs £32 to £40 per ton, according to its purity.

POTASSIUM PERCARBONATE: $K_2C_2O_6$. On electrolysing potassium carbonate solution at a very low temperature (— 15°) a bluish deliquescent powder separates at the anode; this is potassium percarbonate formed by the union of two carbonate ions:



$$\begin{matrix} CO_3K \\ \vdots \\ CO_3K \end{matrix}.$$

At 200° to 300° it is decomposed, forming $CO_3K_2 + CO_2 + O$, and the aqueous solution evolves oxygen at 45°, so that it is a useful oxidising agent and also bleaches various substances. With dilute acids or alkali hydroxides it forms hydrogen peroxide:

$$C_2O_6K_2 + 2HCl = 2KCl + 2CO_2 + H_2O_2$$
$$C_2O_6K_2 + 2KOH = 2CO_3K_2 + H_2O_2.$$

Certain metallic oxides such as Ag_2O, MnO_2, PbO_2, etc., are reduced by it with vigorous evolution of oxygen: $Ag_2O + C_2O_6K_2 = Ag_2 + CO_3K_2 + CO_2 + O_2$.

Solutions of the percarbonate may be titrated with permanganate in acid solution (1 c.c. of normal permanganate = 0·099 grm. of $K_2C_2O_6$).

POTASSIUM SILICATE or **SOLUBLE POTASH GLASS**. Van Helmont obtained this substance as far back as 1610 by melting sand with much potassium carbonate. In 1648 Glauber described a method of preparing it, with full details, and in 1815 Fuchs prepared a compound of silicic acid and potash, which contained an excess of silica and was not deliquescent. It is not known in the crystalline condition and is formed by dissolving silicic acid in solutions of potassium hydroxide. It is obtained industrially by melting quartz sand with potassium carbonate and powdered coal in a furnace (as for sodium silicate). The product is broken up and dissolved in hot water under pressure, forming a heavy liquid which is used for various industrial purposes.

On drying the concentrated solution in the air a solid crust is formed on the surface, which becomes white and opaque and may be redissolved in hot water after pulverisation. The composition of the silicate varies considerably, but usually it corresponds approximately with the formula, $K_2O, 4SiO_2$, though the number of molecules of SiO_2 may vary.

Solutions of potassium silicate deposit silica under the action of the CO_2 of the air.

It is used in the same way as soluble soda glass in cotton printing, for fixing the colours in stereochrome work, for rendering fabrics resistant to fire, for making mastic, etc. Commercial solutions of 30° to 33° Bé. cost £8 per ton, and the solid silicate in lumps costs £20 per ton (for statistics, *see* Sodium Silicate, *below*).

POTASSIUM TRITHIOCARBONATE: K_2CS_3. This is used instead of carbon disulphide against phylloxera (*see* p. 495). It has the advantage over carbon disulphide of not being volatile, therefore undergoing less loss in the soil. The use of sodium or calcium thiocarbonate is more economical, but the potassium salt also acts indirectly as a potash fertiliser. It is prepared in solution (corresponding with 15 per cent. of CS_2) by the action of potassium sulphide on carbon disulphide: $K_2S + CS_2 = K_2CS_3$.

It is slowly decomposed in the soil by moisture and by carbon dioxide with continuous production of carbon disulphide: $CS_3K_2 + CO_2 + H_2O = H_2S + CS_2 + K_2CO_3$.

The commercial value of the yellow liquid is proportional to the percentage of CS_2 which it is capable of yielding. This is determined by heating the thiocarbonate solution and condensing the CS_2 which distils. There are various other more exact analytical methods which we cannot describe here.

POTASSIUM CYANIDE: **KCN** (and **SODIUM CYANIDE**). This compound was formerly obtained in low yield by heating the following mixture in large covered iron crucibles to redness: 8 parts of dry potassium ferrocyanide with 3 parts of dry potassium carbonate and a little carbon, or preferably with a little sodium in order to prevent the formation of potassium cyanate. It is obtained pure by heating potassium ferrocyanide alone in covered iron crucibles:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2;$$

the fused potassium cyanide is decanted from the iron carbide and extracted with alcohol; after evaporation of the solvent the pure salt is melted.

For ten years before 1900 it was prepared by the process proposed by Erlenmeyer in 1876, viz., by melting potassium ferrocyanide with sodium : $K_4Fe(CN)_6 + 2Na = 2NaCN + 4KCN + Fe$; the mixed sodium and potassium cyanides are used directly in practice.

Since 1900 these cyanides have been prepared synthetically in various ways,[1] prin-

---

[1] The following syntheses have been applied practically: Siepermann (Ger. Pats. 51,562, 125,572, and 133,259) passes ammonia at 800° over a mixture of carbon and potassium carbonate and lixiviates the cyanide formed: $K_2CO_3 + NH_3 = CNOK + KOH + H_2O$; $CNOK + C = KCN + CO$. Beilby's process (Ger. Pat. 74,554), used in England, is similar to the preceding, but yields fused KCN directly by forcing the ammonia through a hot liquid mass composed of 60 per cent. K_2CO_3, 20 per cent. KCN, and 20 per cent. of powdered charcoal; by this process the Cassel Gold-Extracting Company, of Glasgow, produced about one-half of the entire European output of cyanide in 1899 (*see also* Swan and Kendall, Ger. Pat. 244,495, who use an excess of carbon and nitrogen directly). In the Castner process (Ger. Pats. 90,999 and 149,678) dry ammonia is passed over fused sodium at 400°, the resulting sodamide (NH_2Na) being mixed with powdered carbon at 550° to 600° to transform it into disodium cyanamide, Na_2N_2C, which at 800° gives almost pure sodium cyanide: $2NH_3 + 2Na = H_2 + 2NH_2Na$, $2NH_2Na + C = Na_2N_2C + 2H_2$, and, according to Drechsel, $Na_2N_2C + C = 2NaCN$. For these reactions use is made of a special iron boiler (*A*, Fig. 211) of rectangular section (III, IV, Figs. 212 and 213) and divided into a number of chambers by partitions protruding from the cover (*C*, Fig. 211 in section, Fig. 212 in plan), the gas being thus forced along an extended zigzag path so as to pass over the surface of the fused mass without bubbling into it (the level is fixed by the walls *G*, *G′* and *H* fixed in the bottom, and *G* carries a row of orifices at the bottom); the fused sodium enters through the vessel *D*, and when it issues from *I* it is stopped and the corresponding quantity of NH_3 passed in from *N*, the amide formed passing to the bottom to be discharged at the cock *K* (*see also* Ger. Pats. 117,623, 124,997, 126,241, and 148,045 of 1901). The Marguerite process was mentioned on p. 366 (*see also* Ger. Pat. 149,594), and that of Frank and Caro on cyanamide on p. 368; with water in the hot, calcium cyanamide gives dicyanodiamide: $2CaN_2C + 4H_2O = 2Ca(OH)_2 + (CN.NH_2)_2$, which crystallises from water in white scales melting at 250° (soluble in alcohol, insoluble in ether), and when fused with sodium carbonate and carbon gives ammonia and sodium cyanide: $(CN.NH_2)_2 + Na_2CO_3 + 2C = N + 3CO + H + NH_3 + 2NaCN$.

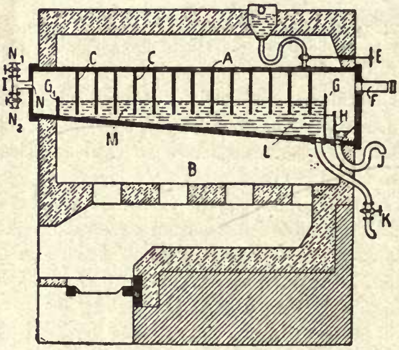


FIG. 211.

It has further been proposed that the calcium cyanamide be fused directly with NaCl, the mass lixiviated with water, and the solution acidified and heated to expel the free HCN, which is fixed by means of sodium hydroxide solution.

In order to free the sodium cyanide from the carbon and sodium carbonate still present, it is lixiviated with a little water at 33°, the solution then containing much NaCN and little soda; the residue is treated with a fresh quantity of water, which dissolves all the remaining NaCN and some soda. These solutions are used to extract fresh portions of the crude cyanide until they are saturated (at 33° the saturated solution contains 517 grms. of NaCN and 26 grms. of Na_2CO_3 per litre), and if they are now concentrated in a vacuum, pure crystallised sodium cyanide free from soda separates, as is seen from considerations analogous to those governing the separation of pure KCl from carnallite (*see* diagram on p. 535 and Ger. Pat. 111,154).

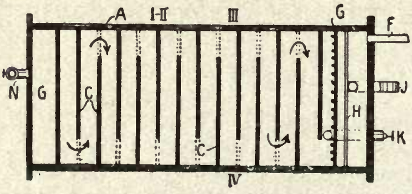


FIG. 212.

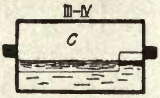


FIG. 213.

In 1843 Zeise obtained ammonium thiocyanate by prolonged heating of carbon disulphide and alcoholic ammonia, followed by distillation of part of the liquid: $CS_2 + 4NH_3 = (NH_4)_2S + NH_4CNS$, this crystallising from the residue of the crystallisation. Claus in 1839 showed that the sulphur of thiocyanates may be eliminated by oxidising agents, with formation of cyanides, and in 1858 Hadow showed that this transformation is almost quantitative. In 1860 Gelis, in France, had carried out the industrial preparation of thiocyanates from CS_2 and ammonium sulphide; at first ammonium trithiocarbonate is formed: $CS_2 + 2NH_4HS = H_2S + CS_3(NH_4)_2$, and this with K_2S at 100° gives: $2CS_3(NH_4)_2 + K_2S = 3H_2S + 2NH_4HS + 2CNSK$.

cipally from sodamide by the processes of Castner and of the Scheideanstalt of Frankfort (*see* Footnote): 70 kilos of wood charcoal are heated at 500° in an iron crucible in presence of a slow current of ammonia, 115 kilos of sodium being then added, the stream of ammonia accelerated and the temperature raised to 600°; the sodiocyanamide formed (*see later*) is transformed almost quantitatively at 800° into sodium cyanide. When the price of sodium was lowered (*see later*), this synthesis rendered it possible to lower the price of the cyanide from £160 to £68 per ton. Potassium cyanide is now made also by the Frank-Erlwein process from calcium carbide and nitrogen (*see* p. 369), and in 1905 10,000 tons were prepared in this way. Further, in various factories, KCN and other cyanides are prepared in various works from the residues of beet sugar molasses.[1]

At that time this product was not required for making KCN, so that it was converted by iron at 150° into potassium ferrocyanide, which was not yet obtained in sufficient quantity from the coal-gas purifiers; the wear of the apparatus was, however, considerable, and the cost of the product too high. In about 1882 Tscherniak and Günzburg (Ger. Pats. 3199 and 16,005) prepared ammonium thiocyanate by heating CS_2 under pressure with aqueous 20 per cent. ammonia: $CS_2 + 2NH_3 = NH_2.CS_2.NH_4 = H_2S + NH_4CNS$; this ammonium salt is decomposed by lime, the ammonia liberated being used again and the calcium thiocyanate employed for the preparation of potassium ferrocyanide. The HCN of impure illuminating gas may be fixed by calcium polysulphides: $CaS_3 + 2HCN = H_2S + Ca(SCN)_2$.

As oxidising agent to eliminate the sulphur, Hood and Salmon (Ger. Pat. 72,644, 1892) used manganese dioxide mixed with lime (residues from the Weldon process, p. 154): $2CS_2 + 2NH_3 + MnO_2 + CaO = 3H_2O + S + MnS + Ca(SCN)_2$; the lime is then precipitated with soda and the MnO_2 regenerated. Raschen (Eng. Pat. 21,451 of 1893) and the British Cyanides Company (Ger. Pat. 81,116) showed that the manganese dioxide is useless, and that the lime and excess of ammonia are sufficient to give a yield of 95 per cent. at 120°: (*a*) $3CS_2 + 2Ca(OH)_2 = CO_2 + 2H_2O + 2CaCS_3$; (*b*) $2CaCS_3 + 2NH_3 = 3HS_2 + CaS + Ca(SCN)_2$.

On the basis of the quantitative transformation of nitrites into ammonium salts by hydrogen sulphide, Tscherniak (Fr. Pat. 248,163) and Gorlich and Wichmann (Ger. Pats. 87,135 and 89,811) obtained thiocyanates by heating a mixture of S, C, H_2S and $NaNO_2$, whilst Goldberg and Siepermann (Ger. Pats. 83,454 and 87,813) obtained them from CS_2, NH_3, sulphites and hydrosulphites.

The elimination of sulphur from thiocyanates to obtain cyanides is effected industrially by the British Cyanides Company (Ger. Pat. 132,294) by means of hydrogen in presence of copper to fix the sulphur: $Cu_2(SCN)_2 + 2Cu + H_2 = 2Cu_2S + 2HCN$, or better by using iron and ferrous chloride (as reducing agent): $2KCNS + 2Fe + FeCl_2 = 2FeS + 2KCl + Fe(CN)_2$; the FeS is then eliminated by acid and the ferrous cyanide treated with alkali. The practical yields are, however, improved if instead of reducing agents use is made of oxidising agents to eliminate the sulphur from thiocyanates (Erlenmeyer had already used permanganate in the analytical process), and according to Alt (1889) good results are obtained with nitric acid in presence of barium chloride to fix the sulphuric acid formed. This process was made practical by Raschen and applied by the United Alkali Company (Eng. Pats. 10,956 of 1895 and 10,476 of 1896): To dilute sulphuric acid heated to 96° in an earthenware vessel is added a mixture of sodium nitrate and potassium thiocyanate, the HCN evolved along with nitric acid and nitric oxide being washed with water at 80° to remove the HNO_3, and the HCN fixed by KOH solution and concentrated to crystallisation; the large amount of NO formed is not absorbed by KOH (if the air is well excluded), and is afterwards mixed with air to form NO_2, which is fixed in a tower by a water spray to regenerate the nitric acid (*see* p. 395). A large amount of cyanide was also made at Runcorn from calcium thiocyanate, which is first converted into the sodium salt, but this process has now been abandoned since it cannot compete with the more economical processes mentioned above—these giving cyanide uncontaminated with nitrites and nitrates.

[1] Vincent's process for preparing trimethylamine (*see* Vol. II., "Organic Chemistry") from beet-sugar molasses (which are rich in betaine, *see* "Organic Chemistry") was modified by Bueb (Ger. Pats. 104,953 and 113,530) and applied in a Dessau works to obtain hydrocyanic acid and cyanides in the following manner: The residue remaining after the alcoholic fermentation of molasses and after removal of the alcohol is concentrated to 42° Bé., and the mass—containing about 4 per cent. of combined nitrogen (12 per cent. of betaine)—subjected to dry distillation at 600° from clay retorts, a residue richer in carbon being thus obtained. The gases which distil consist of H_2O, CO_2, CO, H, CH_4, N_2, NH_3, and methylamine, and are passed into a superheater at 800° to 1000°, after which they have the following composition by volume: 7 per cent. HCN, 7 per cent. NH_3, 8 per cent. CH_4, 12 per cent. H_2, 18 per cent. CO, 24 per cent. CO_2, 24 per cent. N_2, and minimal proportions of naphthalene, acetonitrile, pyridine, etc.; the methylamine is converted by the superheating into the corresponding amount of HCN, but the gases must be rapidly cooled, as otherwise part of the HCN decomposes. Bergmann (1896) and Denis Lange (1897) obtained good yields by heating a mixture of 2 vols. NH_3, 5 vols. N_2, and 50 vols. H_2 to about 1100° in presence of glowing wood charcoal; according to Lange, not only the nitrogen of the ammonia, but also part of the free nitrogen is transformed in this way into HCN or ammonium cyanide; thus, the presence of hydrocarbons is apparently not indispensable for obtaining HCN. Voerkelius (1909) showed that with such mixtures and with wood charcoal at 700°, methane is not formed, and the best yields are obtained at 1000° with illuminating gas instead of hydrogen as a diluent of the ammonia (the yield is also related to the dilution of the

It forms a white crystalline mass of alkaline taste [Don't taste! It is extremely poisonous.—*Translator*]; it smells of bitter almonds, hydrocyanic acid being set free by the CO_2 of the air. It is very soluble in water and slightly so in alcohol; it is very poisonous, although certain animals, such as horses, mules, and pigs, resist fairly strong doses. It is much used in electro-plating baths and in large quantities for the extraction of gold (*see* Gold). (*Translator's note.*—Sodium cyanide is to-day exclusively used for this purpose.)

In 1909 Germany exported 6282 tons of potassium and sodium cyanides. The imports exceeded the exports by 1120 tons in 1895 and by 6300 tons in 1909.

A factory erected in Sweden in 1910 produces annually 500 tons of cyanide for the extraction of gold in S. Africa.

England exported 7000 tons of potassium and sodium cyanides in 1909 and 7500 (£640,000) in 1910.

The cyanides produced in the United States in 1912 were valued at £7,200,000.

In 1890, before the Forrest process for the extraction of gold was used, the world's production was only 100 tons, this being used for galvanic gilding, silvering, and nickel-plating.

Potassium Cyanide is also obtained to-day from beetroot residues (*see* note on p. 549). The commercial product containing 30 per cent. costs £44 per ton. When of 60 per cent. purity it costs £74, and of about 98 per cent. purity £86. The carbide process has greatly reduced the price: pure, for laboratory purposes, it costs 17*s*. 6*d*. per kilo.

An important group of compounds derived from cyanogen and ferro- and ferri-cyanides is described later, in the chapter dealing with iron, and another group—not less important—of the derivatives of cyanic acid, NC.OH; cyanuric acid $(NC.OH)_3$; thiocyanic acid, NCSH, and thiocyanuric acid $(NC.SH)_3$, in Vol. II. ("Organic Chemistry").

POTASSIUM PHOSPHATES. Three phosphates are known, K_3PO_4, K_2HPO_4, and KH_2PO_4, and are obtained by the action of phosphoric acid on potassium carbonate. They are of little practical importance, and are not obtained in a well-crystallised condition, the corresponding sodium salts being usually preferred for practical purposes.

POTASSAMIDE: KNH_2. This compound is obtained by passing a current of dry ammonia over molten potassium and forms a blue liquid which yields a white crystalline mass on cooling. It sublimes at 400° and then dissociates into its elements. With water it forms NH_3 and KOH.

GENERAL CHARACTERISTIC REACTIONS OF POTASSIUM SALTS

The potassium salts are almost all soluble in water although their solutions give a white crystalline, only slightly soluble, precipitate of potassium hydrogen tartrate with tartaric acid. Chloroplatinic acid, H_2PtCl_6, gives a yellow crystalline precipitate of potassium platinichloride, K_2PtCl_6. This compound is only slightly soluble in water and still less so in alcohol.

Potassium fluosilicate and potassium perchlorate are also only slightly soluble and may be used for separating potassium from other metals. All potassium salts give a

---

ammonia): $NH_3 + C = HCN + H_2 - 39{\cdot}5$ Cals. and $2C + H_2 + N_2 = 2HCN - 59{\cdot}7$ Cals. The concentration of HCN is a maximum (up to 40 per cent.) at above 3000°, and as the temperature is lowered dissociation occurs (as for nitric oxide, *see* p. 391). Voerkelius showed further that between 800° and 1000° trimethylamine and dimethylamine are decomposed to the extent of 98 per cent.: $N(CH_3)_3 = HCN + 2CH_4$ and $NH(CH_3)_2 = HCN + CH_4 + H_2$; dilution with hydrogen diminishes the yield in either case: $NH(CH_3)_2 + 2H_2 = NH_3 + 2CH_4$. At 720° the yield of HCN is small and at 600° zero. The material of the superheater and various catalysing substances may diminish the yield of HCN.

The gases from the rapidly cooled molasses residue are passed into sulphuric acid to fix the free ammonia and the little pyridine present, whilst the HCN is absorbed by water and then transformed into sodium cyanide. In the tubing in which gases containing HCN circulate a slight suction is always maintained, in order that poisonous gases may not escape into the air. The unabsorbed gases are burnt to heat the retorts. The slightly alkaline aqueous sodium cyanide solution is concentrated in a vacuum and finally the crystalline anhydrous cyanide is precipitated above 30°, whilst below 30° it crystallises with water, $NaCN + 2H_2O$. The crystals are centrifuged, dried, and compressed into small blocks, the strength being 120 to 125 per cent. (calculated as KCN, although part is NaCN). About 35 to 40 per cent. of the nitrogen of the molasses residues is converted into NaCN and about 25 per cent. into NH_3, while about 35 to 40 per cent. is lost as free nitrogen.

pale violet coloration to the Bunsen flame and a spectrum containing two characteristic lines, red and violet, showing that at high temperatures all salts of potassium dissociate, forming potassium ions which give this general reaction.

RUBIDIUM: Rb, 85.45, and CAESIUM: Cs, 132.81

These metals are not abundant but are fairly widely diffused in nature, and often accompany potassium in saline waters and in the ashes of plants.

Rubidium is found as an impurity (0·5 per cent.) in the mineral *lepidolite:*

$$K_4Li_4(AlF_2)_3Al_4(Si_3O_8)(SiO_4)_3,$$

and also in the *carnallite* of Stassfurt; caesium is found in a very rare sulphate of aluminium and caesium called *pollucite*: $H_2Cs_4Al_4(SiO_3)_9$. These metals were discovered as elements by Bunsen and Kirchhoff in 1860 by means of the spectroscope. Rubidium and caesium salts are more insoluble than those of potassium, so that they may be separated from the latter.

The elements are obtained in the free metallic state on electrolysing their respective fused chlorides. They are also obtained from the corresponding hydroxides by heating them in an iron tube, together with magnesium or aluminium, in a current of dry hydrogen:

$$2RbOH + 2Mg = 2Rb + 2MgO + H_2.$$

The metals distil and are collected in petroleum.

Rubidium and caesium have a silvery appearance, but are easily oxidised by the air, Rb forming a *peroxide*, Rb_2O_4. Rubidium has a specific gravity of 1·52 and melts at 38·5°; when thrown into water it catches fire with a violet flame. Caesium has a specific gravity of 1·85, melts at 26·4°, and readily catches fire in the air; it boils at 270°.

Rubidium iodide is now sometimes used in medicine instead of potassium iodide.

In contradistinction to potassium, rubidium and caesium form many halogen derivatives in which they act as polyvalent elements: $RbClBr_2$, $RbBr_3$, $CsBr_3$, CsI_5. The compound, $RbICl_4$, is a yellow solid obtained by treating a solution of rubidium iodide with chlorine, and is slightly soluble in water; the solution is a powerful oxidising agent, and dissolves gold and platinum.

Caesium platinichloride is very insoluble in water and may thus be separated from the potassium salt.

Rubidium and caesium cost about £1 per gram.

SODIUM: Na, 23

Sodium is not found in the free state in nature on account of its great reactivity, but is widely diffused in the combined state in numerous minerals, such as *cryolite, borax, glauberite*, etc. It is still more abundant in the form of sodium chloride, which is found in important geological strata in the form of *rock salt;* it is very abundant in sea water, which contains up to 3 per cent. of sodium chloride. It is also found in large quantities in the form of nitrate as *Chili saltpetre.* In vegetable organisms potassium salts ordinarily predominate, whilst in animal organisms there is a preponderance of sodium salts.

It was obtained free for the first time by Davy in 1807 by the electrolysis of fused sodium hydroxide. After 1855 it was prepared industrially by heating a mixture of sodium carbonate, coal, and a little limestone in iron retorts by Deville's method:

$$CO_3Na_2 + 2C = 3CO + Na_2.$$

In 1886 Castner obtained it by a greatly improved method, employing sodium hydroxide and coal mixed with iron carbide, the latter being used to decompose the water which is formed. The reduction of the sodium hydroxide needs a much lower temperature than that of the carbonate, so that there is an economy of fuel, and the apparatus is attacked less. Before 1850 1 kilo of sodium cost about £80. After the introduction of Castner's process the price was lowered to less than 8*s*., and it then became possible to use sodium industrially for the preparation of aluminium, but great improvements have now been made in that industry, rendering it independent of the use of sodium, which was always very dear.

In 1898 Netto obtained better results by dropping molten sodium hydroxide contained in *a* (Fig. 214) over red-hot coal contained in a cylindrical vertical retort, *g*. Vapours of sodium are continuously evolved at the top and condensed in the iron vessels, *k*, the fused sodium being collected under petroleum in the vessel, *l*. In the lower part of the retort, at *I*, molten sodium carbonate continuously escapes:

$$4NaOH + 2C = CO_3Na_2 + Na_2 + CO + 2H_2.$$

An ingenious furnace for the electrolytic preparation of sodium, the walls serving as anode, was suggested by Scheitlin (Ger. Pat. 248,873, 1910).

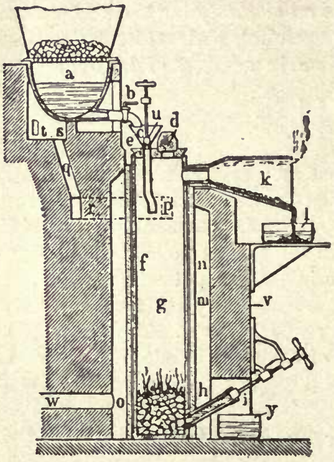


FIG. 214.

Sodium is prepared to-day solely by the electrolysis of molten sodium chloride, employing a cathode of molten lead, with which the free sodium forms an amalgam; this is passed into a second compartment in which molten sodium hydroxide is present as an electrolyte. The amalgam then acts as an anode, and the sodium is deposited at the cathode without any consumption of NaOH. This process is a happy combination of that of Acker (*see below* under Electrolytic Caustic Soda) with that patented by J. Castner in 1891. By the latter process sodium is obtained by the electrolysis of fused sodium hydroxide (this process is still used in England and in France). At Niagara the combination of the two processes gives excellent results and the sodium costs less than 1*s*. 2*d*. per kilo.

The energy consumed is about 13 kw.-hours per kilo of sodium, the current yield being about 50 per cent.

According to an American patent of 1901 electrical energy is greatly economised by melting a mixture of equal parts of NaOH and sodium sulphide; a low voltage then suffices for the decomposition of the Na_2S alone, which yields sodium, whilst the nascent sulphur immediately forms Na_2S at the cost of the NaOH. In this process it is only necessary to add NaOH continuously in order to obtain as much free sodium as is contained in the hydroxide. According to a patent of 1914 almost one-half of the current is saved by electrolysing a mixture of NaOH with 17 per cent. of Na_2CO_3, the melting-point being then lowered to 280°; the yield may be kept high by frequent changing of the electrode, which becomes rusty by the action of impurities and is then replaced by a fresh smooth one (Ger. Pats. 224,852 and 224,853, 1908).

In the *laboratory* it is prepared by heating sodium peroxide with wood charcoal or with calcium carbide:

$$3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na.$$

PROPERTIES. Metallic sodium has a silvery appearance similar to that of potassium; it has the density 0·97, melts at 97·6°, and boils at 742°, forming colourless vapours which burn with a yellow flame. It oxidises in the air, and on throwing a piece of sodium on to water it travels over the surface and decomposes without catching fire, because it evolves less heat than potassium; if, however, its movement over the water is hindered by enclosing it in a piece of paper it catches fire because the kinetic energy is then also transformed into thermal energy. It is soluble in absolute alcohol with evolution of hydrogen, forming sodium ethoxide.

Sodium is used for the preparation of silicon, magnesium, sodium peroxide and cyanide, sodamide and certain dyestuffs. Until the year 1880 large quantities of sodium were used for the preparation of aluminium, but it is no longer used for this purpose. A certain amount is used for desulphurising petroleum.

In 1865 sodium cost £2 8*s*. per kilo, but at present it costs less than 4*s*.

The world's production, which is divided almost equally between England, Germany, and the United States, was estimated at 350,000 tons in 1905, and the sale price at the works for large quantities sank to less than 2*s*. per kilo. The price will possibly become still lower in the future if the direct preparation from sodium chloride by Acker's process is successful.

SODIUM MONOXIDE : Na_2O. This compound was not known until a short time ago; it is now prepared from sodium and sodium nitrate in the manner already explained in the case of potassium oxide. Barium nitrate or nitrite may also be used (Ger. Pat. 144,243 of 1903).

SODIUM PEROXIDE : Na_2O_2. This is prepared in Castner's apparatus (1891) by heating sodium to 300° in aluminium trays (Fig. 215) contained in an iron retort, *B*, and passing over it a current of dry air free from CO_2.

Na_2O_2 is formed also by heating a mixture of 100 parts of the nitrate, $NaNO_3$, and 80 parts of magnesia, MgO, or lime, CaO. Nitrous vapours are first evolved, and oxygen and nitrogen are then evolved at a red heat; the remaining mass is heated further to about 400° in a current of dry air free from CO_2. On pouring the mass into cold water a solution of sodium peroxide is obtained which may be employed as such, whilst part of the magnesia or lime separates.

It forms a slightly yellowish white mass which gives off oxygen only at high temperatures, whilst it dissolves in water with evolution of heat, forming oxygen which is liberated by the heating. With water it forms a hydrate, $Na_2O_2, 8H_2O$.

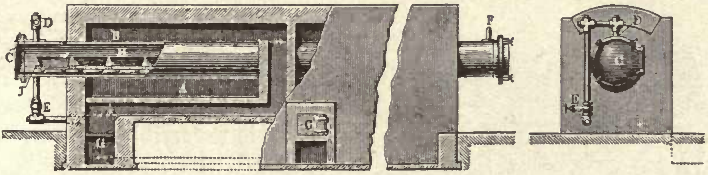


Fig. 215.

It is an energetic oxidising agent, which, on heating, carbonises many organic substances in the absence of water; at red heat it has an oxidising power superior to that of all other oxidising agents.

It is advantageously used in aqueous solution for bleaching textile fibres; in the case of animal fibres which are affected by alkalis (silk and wool) it must be remembered that with water NaOH is also formed which must be gradually neutralised, as it is formed, by the corresponding quantity of sulphuric or acetic acid:

$$Na_2O_2 + H_2O = 2NaOH + O.$$

When it is poured into water the reaction is sometimes so violent that flame is produced; Gruner (1910) avoids this difficulty by first mixing the sodium peroxide with a little carbon tetrachloride, which also renders the evolution of oxygen more regular.

It may be used in diving-bells and generally in close inhabited spaces in order to keep the air pure; since a man consumes 25 litres of oxygen per hour, he can be kept alive with 1 kilo of Na_2O_2 for more than five hours.

Sodium peroxide costs 2*s*. 4*d*. to 2*s*. 10*d*. per kilo, and is placed on the market under the name "oxone."

ANALYSIS OF Na_2O_2 : The commercial value depends on the quantity of active oxygen which it is capable of yielding. Its strength cannot be determined by titrating with permanganate. The best results are obtained by Archbutt's method: 1 grm. of sodium peroxide is decomposed in Lunge's nitrometer with 15 c.c. of water and two drops of a strong solution of cobalt nitrate; the oxygen liberated is then measured. A particular sample gave 132·6 c.cm. of oxygen = 0·1895 grm.

SODAMIDE, NH_2Na is obtained by passing dry ammonia over fused sodium. It forms a crystalline mass which melts at 120° and if powdered charcoal is then poured into it, sodiocyanamide is first formed: $2NaNH_2 + C = 4H + Na_2N_2C$; this at a higher temperature is transformed into sodium cyanide: $Na_2N_2C + C = 2NaCN$. Sodamide is used for the synthesis of the cyanides (*see* p. 549) and also in the synthesis of indigo (*see* Vol. II., "Organic Chemistry").

SODIUM HYDROXIDE: NaOH (CAUSTIC SODA)

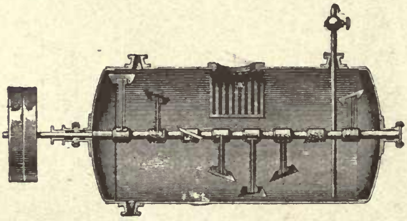
PROPERTIES. When cooled, fused sodium hydroxide forms a white mass of radiating crystals of sp. gr. 2.

It melts at a red heat, and decomposes at about 1200° to 1250° into Na, H and O. In order to obtain pure sodium hydroxide it is melted in vessels of silver and not of other metals, which are easily attacked (even Pt).

It is decomposed by electrolysis, sodium separating at the negative pole (cathode). It is very soluble in water with evolution of heat (*see* Table), and is deliquescent in the air, from which it rapidly absorbs carbon dioxide. The chemical properties are similar to those of caustic potash.

Solutions concentrated in the cold deposit various hydrates: from $NaOH, H_2O$ to $NaOH, 7H_2O$.

PREPARATION BY CHEMICAL METHODS. Since 1853, especially in England, sodium hydroxide has been prepared by Gossage's method, from dilute (10 per cent.) boiling solutions of crude sodium carbonate, by immersing in them boxes containing quicklime, and stirring the boiling liquid continuously. If the sodium carbonate solution is more concentrated the yield is lower, because the reaction is reversible. Thus, with solutions of 5 per cent. Na_2CO_3 (5° Bé.), more than 99 per cent. of the carbonate is transformed into the hydroxide, whilst on starting from a solution of 20 per cent. (23° Bé.) only 90 per cent. of the carbonate is so transformed. The reaction occurs even in the cold, but is then slower and less complete. It is preferable to work in the hot, although about 2 per cent. is then lost in the form of *Gaylussite* ($Na_2CO_3, CaCO_3, 5H_2O$), which is insoluble and is not decomposed by water. The most favourable equilibrium for the production of NaOH is at 80°, and it is slightly less favourable at 106° to 110°. Theoretically 53 kilos of CaO correspond with 100 kilos of Na_2CO_3; in practice a little more lime is used, which is slaked directly in the solution of the sodium carbonate.


FIG, 216.

The reaction occurs more easily with Na_2CO_3 than with K_2CO_3.

The operation is carried out in vertical iron cylinders (Lunge), or in horizontal cylinders (Solvay), as shown in Fig. 216:

$$CaO + H_2O + Na_2CO_3 = CO_3Ca + 2NaOH.$$

A stirrer or an air injector prevents the lime from depositing. The liquid is filtered from the insoluble calcium carbonate, when it is found by means of HCl that the clear solution no longer contains sodium carbonate (evolution of CO_2).

Prior to the electrolytic preparation (*see later*), almost the whole of the caustic soda was prepared by the Leblanc method from NaCl (*see later*, Sodium Carbonate). The concentration of the solutions is dealt with later.

The Löwig process allows of the preparation of caustic soda or potash by the hydrolysis of sodium or potassium ferrite, obtained by heating ferric oxide and the alkali carbonate to a high temperature in a round furnace similar to that used for the Leblanc process. It was proposed in 1880, improved in 1887 (Ger. Pat. 41,990), transferred to the Solvay

Company and applied practically just before the start of the European War: $Fe_2O_3 + Na_2CO_3 = CO_2 + Na_2O, Fe_2O_3$; 400 kilos of Fe_2O_3 and 106 kilos of Na_2CO_3 are used in order that caustic soda free from carbonate may be obtained. When cold, the ferrite, obtained in black, shiny granules (if grey or greenish, they still contain sodium carbonate), is introduced into a battery of lixiviators similar to the diffusers used in the sugar industry (*see* Vol. II.) and the sodium hydroxide is extracted with water at 50° to 60° so as to obtain a 23 to 24 per cent. solution. After clarification, this solution is concentrated *in vacuo* to 45° Bé.: $Na_2O, Fe_2O_3 + 4H_2O = 2NaOH + 2Fe(OH)_3$, the ferric hydroxide being dried and used again.

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF SOLUTIONS OF SODIUM AND POTASSIUM HYDROXIDES

Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of NaOH	Per cent. by weight of KOH	Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of NaOH	Per cent. by weight of KOH
1·007	1	0·61	0·9	1·252	29	22·64	27·0
1·014	2	1·20	1·7	1·263	30	23·67	28·0
1·022	3	2·00	2·6	1·274	31	24·81	28·8
1·029	4	2·71	3·5	1·285	32	25·80	29·8
1·036	5	3·35	4·5	1·297	33	26·83	30·7
1·045	6	4·00	5·6	1·308	34	27·80	31·8
1·052	7	4·64	6·4	1·320	35	28·83	32·7
1·060	8	5·29	7·4	1·332	36	29·93	33·7
1·067	9	5·87	8·2	1·345	37	31·22	34·9
1·075	10	6·55	9·2	1·357	38	32·47	35·9
1·083	11	7·31	10·1	1·370	39	33·69	36·9
1·091	12	8·00	10·9	1·383	40	34·96	37·8
1·100	13	8·68	12·0	1·397	41	36·25	38·9
1·108	14	9·42	12·9	1·410	42	37·47	39·9
1·116	15	10·06	13·8	1·424	43	38·80	40·9
1·125	16	10·97	14·8	1·438	44	39·99	42·1
1·134	17	11·84	15·7	1·453	45	41·41	43·4
1·142	18	12·64	16·5	1·468	46	42·83	44·6
1·152	19	13·55	17·6	1·483	47	44·38	45·8
1·162	20	14·37	18·6	1·498	48	46·15	47·1
1·171	21	15·13	19·5	1·514	49	47·60	48·3
1·180	22	15·91	20·5	1·530	50	49·02	49·4
1·190	23	16·77	21·4	1·546	51		50·6
1·200	24	17·67	22·4	1·563	52		51·9
1·210	25	18·58	23·3	1·580	53		53·2
1·220	26	19·58	24·2	1·597	54		54·5
1·231	27	20·59	25·1	1·615	55		55·9
1·241	28	21·42	26·1	1·634	56		57·5

ELECTROLYTIC PREPARATION. Considerable quantities of sodium hydroxide are to-day obtained electrolytically, starting from solutions of sodium chloride or from fused sodium chloride. The sodium is obtained in the form of sodium hydroxide, and all the chlorine is absorbed by slaked lime and goes into commerce as chloride of lime (bleaching powder) containing 35 to 37 per cent. of Cl.

It was once believed that in the electrolytic decomposition of an aqueous solution of sodium chloride, only the following reactions occur:

$$NaCl = Na + Cl; \quad Na + H_2O = NaOH + H,$$

so that caustic soda and hydrogen should be obtained at the negative pole (cathode) and only chlorine at the positive pole (anode). It is found in practice, however, that oxygen is developed at the anode and that sodium hypochlorite and chlorate, and even perchlorate, are formed in solution. Forster and Müller in 1903 studied all the conditions under which these secondary reactions occur, and it only then became possible to regulate, and more or less to eliminate, this difficulty. The difficulties are always serious and numerous, but the process is sufficiently important to claim the continual attention of students and of technologists concerned in increasing the value of the chloride by transforming it into the alkali hydroxide by means of the simple action of the electric current.

Theoretically one ampère-hour should produce 1·322 grms. of chlorine and 1·491 grms. of NaOH. It should be noted that the same quantity of electrical energy produces a greater weight of potassium hydroxide of molecular weight 56 than of sodium hydroxide of molecular weight 40, although the quantities of chlorine remain the same in both cases. The electrolytic process is thus of greater advantage in potassium hydroxide manufacture.

The electrolytic processes may be divided into three groups : the electrolysis of aqueous solutions of sodium chloride, with and without diaphragms, and electrolytic decomposition of molten sodium chloride.

The material of which the electrodes are constructed is of great importance in the electrolytic processes because it has to resist the action of the alkali and of the nascent chlorine. Those formed of compact retort graphite serve very well, although the large consumption of electrodes does not depend on the action of the reagents only, but largely on the intensity of the electric current. Electrodes of powdered and sheet platinum have yielded good results, but a net of platinum wire which costs relatively little has given still better results. To-day, however, the electrodes generally used are made of artificial graphite produced by the firm of Acheson at Niagara (*see* Graphite, p. 440). When carbon electrodes are used there is evolution of carbon dioxide at the anode which causes loss of sodium hydroxide, and it is therefore necessary to interrupt the electrolysis when the solution contains 8 per cent. of sodium hydroxide. In order to avoid the formation of carbon dioxide anodes of ferrosoferric oxide are prepared which, however, melt with difficulty at 2000° to 3000°, and need to be carefully cooled in order to avoid the formation of cracks.[1] These anodes are not attacked by oxygen, and thus cause the oxidation of the chloride to chlorate, which is hence obtained gratuitously. The sodium hydroxide solution obtained by this process by the Elektron Company of Griesheim (*see below*) is concentrated up to 50 per cent. At this point, however, it acquires a yellow colour from the presence of iron; the elimination of the latter substance is easily carried out by an osmotic process without the use of a membrane, by allowing the solution to diffuse into water running in the opposite direction in long channels.

Diaphragms constructed of porous earthenware (*see below*) are used to keep the products of the electrolytic decomposition separate. Otherwise hypochlorites or chlorates would be formed by the interaction of the sodium hydroxide and the chlorine. The spaces in which the anodes and the cathodes are disposed are thus separated without prevention of the passage of the current. It was not, however, an easy matter to prepare such diaphragms, which must be resistant to the corroding action of the chlorine and alkali.

To these technical difficulties a grave commercial difficulty was added, which consisted in the excessive quantities of chloride of lime which were obtained compared with the quantity of sodium hydroxide, these being in the proportions of about 2·5 to 1. There was not a sufficient demand for the former product, and the price therefore descended in recent years from £8 to £3 12*s*. per ton, the commercial basis of the whole industry being thus endangered. To-day, however, the price has risen (in Italy) to £5 12*s*. per ton, through an arrangement between the producers and through the protective tariffs.

In many quarters a suggestion has been made to utilise the chlorine for the production of hydrochloric acid, thus reversing the process used until now of obtaining chlorine from hydrochloric acid. The transformation of sodium hydroxide into carbonate has also been proposed because there is a greater demand for the latter. These projects, however,

---

[1] Besides the diaphragms of cement and asbestos mentioned later and used especially for the electrolysis of potassium chloride, the Elektron Company of Griesheim obtained marked success with electrodes of magnetic oxide of iron (Ger. Pats. 157,122 and 193,367). Similar electrodes are those prepared according to Ger. Pat. 211,300, viz. by burning iron in a current of oxygen, fused magnetic oxide being thus obtained.

although technically possible, have not been applied, because they collide with the thermochemical balance of their manufacture; thus, more energy is required in order to transform sodium chloride into sodium hydroxide and chlorine than to transform it into carbonate and hydrochloric acid; there would therefore be a waste of energy in passing from the hydroxide to the carbonate and from chlorine to HCl, which can, on the other hand, be obtained by simple chemical processes with less consumption of energy. The chlorine is now used to some extent for the manufacture of carbon tetrachloride (*which see*), and a portion of the chlorine is placed on the market in the liquid state. The electrolytic process should only be used to satisfy the demand for chlorine and sodium hydroxide. To-day, after the great growth of aeronautic enterprise, the collection of the hydrogen which is evolved at the negative pole in large quantities has also been taken in hand. The caustic potash works of Griesheim alone produce 6000 cu. metres of hydrogen daily.

I. PROCESSES WITHOUT DIAPHRAGMS. The great difficulties which were first encountered in applying electrolytic processes with diaphragms led Castner in America, Kellner in Austria, and Sinding-Larsen in Norway almost simultaneously to devise processes without diaphragms, based on the employment of metallic mercury as a cathode and conducting the electrolysis of the salt solution in such a manner that the sodium cation is immediately dissolved by mercury at the instant of its formation, forming an amalgam. This is then passed into water outside the apparatus, where a somewhat concentrated solution of pure sodium hydroxide, almost free from chlorides, is obtained with evolution of hydrogen and regeneration of mercury, which is then again pumped into the apparatus.[1]

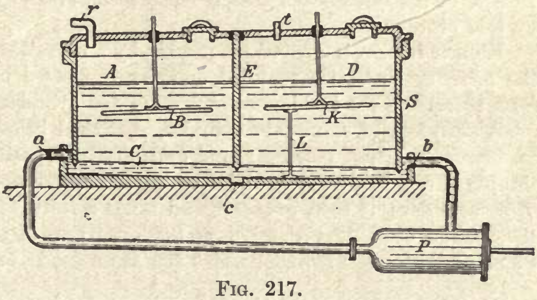


FIG. 217.

A simple diagram of one of these forms of apparatus, the first one used by Kellner, is shown in Fig. 217. The stoneware vessel, *S*, with a slightly inclined bottom, is divided into two cells by the partition, *E*. In the cell *A* we have the anode, *B*, formed of iridio-platinum plates or gauze immersed in a concentrated solution of sodium chloride. The mercury, *C*, at the bottom acts as a cathode and combines with the sodium to form an amalgam; this sodium is then utilised and the mercury regenerated in the cell *D*, where there is a cathode, *K*, of iridio-platinum immersed in water. This decomposes the amalgam, forming NaOH and hydrogen, which is evolved at the cathode, *K*, whilst the mercury liberated acts as an anode and is pumped into the first cell, *A*, by the pump, *P*. Since a small part of the amalgam is already decomposed in the cell *A*, the anodic oxygen in *D* is formed in presence of less alkali than corresponds with the evolved hydrogen, so that a small portion of the mercury in *D* is oxidised. Kellner overcame this difficulty by introducing between the cathode, *K*, and the anode (amalgam) a secondary electrode, *L*, formed of a metallic spiral, thus establishing a short circuit in such a manner that external work was avoided, but sufficient to accelerate the solution of the sodium in the mercury, thus removing it more easily and more rapidly from the action of the aqueous solution of the salt.

In England, and in America (at Niagara), the Castner process was applied and unites those of Kellner and Solvay into a single process. There are three parallel cells (Figs. 218 and 219) separated by a mercury seal; at the bottom of the cells the depth of the mercury is a few millimetres. In the lateral cells, *b*, the solution of sodium chloride is contained together with the anodes; the amalgam from each lateral cell in turn is treated in the central cell, which contains water, by means of the gentle raising and lowering produced at one extremity of the apparatus by means of an eccentric, *E*.

A similar plant is working at Niagara Falls with a current efficiency of 90 per cent. and

---

[1] Patents for the various modifications of this process are numerous, and it will suffice to mention here those of Atkins, 1892; Hermite, 1893; Vautin, 1894; Kellner, 1893 and 1896, etc.; Castner, 1894, 1896, etc.; Störmer, 1897; Rhodin, 1899; Solvay, 1899, etc. In these processes good yields are obtained with high current densities.

consuming 6000 h.p.; 50 tons of salt are treated daily, producing 36 tons of sodium hydroxide of 97 to 99 per cent., and about 90 tons of chloride of lime containing 36 per cent. of chlorine.

In 1899 Solvay (Ger. Pat. 100,560) discovered a means of working with less mercury by making use of the lower specific gravity of the amalgam, which floats at the top and is continuously discharged as a fine coating, this being formed at the surface, without circulating large masses of mercury. The electrolysis is conducted in two parallel vats in communication with one another and so arranged that a bucket-wheel raises the mercury and keeps it in continuous circulation. The batteries of this plant are suitable for currents of 10,000 to 15,000 amps. The factories of Jemappes in Belgium, of Ljubimoff in Russia, of the Società del Caffaro at Brescia, and of the Rumianca works (Novara) work by this process.

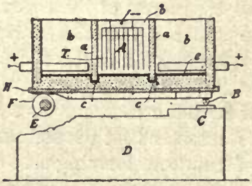


Fig. 218.

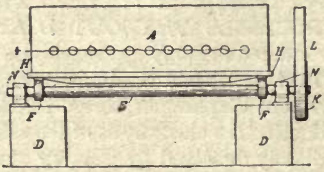


Fig. 219.

Kellner further improved his process by a most ingenious apparatus (Fig. 220), in which the mercury circulates round a cylinder immersed in the bath through channels which form spirals on the inside and outside of the cylinder alternately.

A porcelain or stoneware cylinder, *A*, closed below, is provided with a channel which forms a spiral, first passing round once at the top along the internal wall, and then continuing through a hole, *c*, and forming a second spiral round the external wall of the same cylinder; it then re-enters and takes a third turn round the inside, a fourth round the outside, etc., until it arrives at the lower part of the cylinder. Inside the cylinder, *A*, there is a bottomless cylinder which acts as an anode, and is filled with solid sodium chloride.

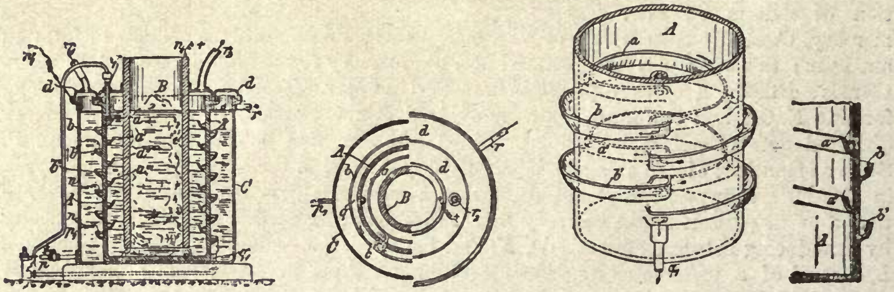


Fig. 220.

The space between the cylinders, *A* and *B*, is filled with a concentrated solution of sodium chloride, whilst the cylinder, *A*, is surrounded by water contained in an iron cylinder, *C*; the mercury passes in through the tube *q*, from which it passes into the channel, *a*, and is in contact at several points with the negative pole (cathode) as it flows slowly round the spiral. Inside the cylinder, *A*, the mercury becomes covered with sodium amalgam, which is produced by the electrolytic decomposition of the NaCl, but when, on continuing its course, it enters the channel which passes along the external wall of *A*, it immediately forms sodium hydroxide in contact with the water, and the mercury is regenerated and again enters the interior of *A* in order to form further sodium amalgam, which is decomposed outside, and so on. In the interior of *A* chlorine is continuously developed and escapes from the tube r_2, whilst outside *A* a solution of sodium hydroxide is formed which gradually increases in concentration and is discharged by a cock; the hydrogen escapes by the tube r_1. The apparatus is closed above by the cover, *d*, which carries the tubes for the escaping gases, etc. This apparatus is not suitable for a very large output, for which the Solvay process is preferable.

The caustic soda prepared by the mercury process is purer and is almost free from sodium chloride, as it is formed by the decomposition of sodium amalgam. This process can, however, withstand the competition of diaphragm processes only when the electrical energy costs less than 0·12*d*. per kw.-hour.

The Chemico-Metallurgical Company of Aussig (Austria) keeps the products of the electrolytic dissociation separate, by making use of the different densities of the liquids in the two chambers containing the electrodes. The apparatus may be considered in principle as a type intermediate between those with diaphragms and those without diaphragms, and is shown in Fig. 221. The anode, *a* (positive pole), is formed of a bundle or disc of carbon placed in a bell, *b*, non-conductive and resistant to chlorine, which is immersed in the NaCl solution. The cathodes (negative pole), *c*, are formed of two iron plates. The exact adjustment of the distance of the anode, *a*, from the lower level of the bell is of the highest importance, because the separation of the chlorine from the sodium hydroxide, which is formed in the vat and which escapes from *f*, depends on this adjustment. The liquid at the level of the lower edge of the bell acts almost as a diaphragm. The electrolyte, which is a concentrated solution of NaCl, enters slowly and continuously through the tube *e*, whilst the chlorine gas escapes through the tube *g*; apparently 85 to 90 per cent. of the current is utilised by this process.

The solution which is obtained contains about 10 per cent. of sodium hydroxide and much sodium chloride. On evaporating the liquid almost the whole of the sodium chloride first separates in the solid state, and the concentrated solution of sodium hydroxide is evaporated separately to dryness and then contains only 2 to 3 per cent. of chlorides.[1]

This belljar process made use of about 900 h.p. in 1910, but, although it has undergone various improvements (Ger. Pats. 237,676 and 191,234), it still remains somewhat cumbrous, a 3000-h.p. plant requiring 25,000 bells.

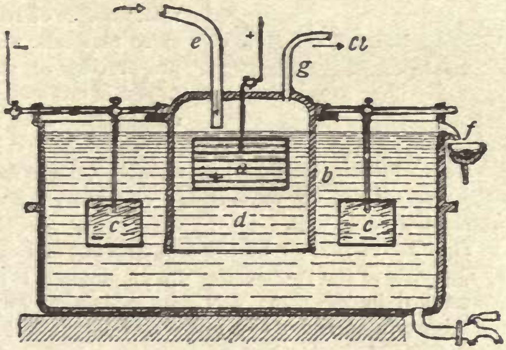


FIG. 221.

II. PROCESSES WITH DIAPHRAGMS. Various German works, now united under the single name of Chemische Fabrik Griesheim-Elektron, commenced experiments on the production of electrolytic soda in 1884, starting from a patent of C. Höpfner, and in 1890 the first European works was erected at Griesheim, using 400 h.p., which was doubled in 1892, and was later increased to 2000 h.p. Since cheap water-power is scarce in Germany, a new plant using 3000 h.p. was erected at Bitterfeld in Saxony in 1893, as cheap lignite is found abundantly in this locality almost on the surface. In 1895 the Bitterfeld establishment was doubled in size, and in 1898 it was absorbed by the Elektron Company. They work with a system of diaphragms, but the details of the process are kept secret. The difficulties encountered in obtaining resistant diaphragms were very great: diaphragms of soap, albumen, parchment-paper, collodium, vulcanite, porous earthenware, limestone, asbestos fabrics, etc., were tried, but all proved useless, these materials being destroyed in a few days. The Elektron Company finally succeeded in preparing resistant diaphragms from porous plates of Portland cement, and lately good diaphragms have also been prepared in America from asbestos fabrics coated with cement

---

[1] In 1896 Kellner proposed to treat the alkaline solution of NaOH directly with carbon dioxide (chimney gases) in order to cause sodium carbonate to crystallise.

The engineer Rambaldini has lately devised a continuous electrolytic process for the preparation of sodium hydroxide without diaphragms, based on the difference in density between the electrolyte and the resulting hydroxide solution, these solutions being superposable without mixing. In spite of repeated experiments on a small industrial scale this process has not yet been accepted by the large caustic soda works as possessing any advantages (Ger. Pat. 183,853 of 1902, granted in 1907).

or sodium silicate. The preparation of the anodes for this process has already been described.

In 1909 several factories (mainly in Germany), especially for the electrolysis of potassium chloride with such diaphragms, were at work, using about 33,000 h.p., this corresponding with a production of 70,000 tons of KOH (*i. e.*, 2·12 tons per h.p.-year). The current yield with this process is about 30 per cent. of the theoretical yield for KOH and less than 25 per cent. for NaOH.

The Badische Anilin-und Soda-Fabrik of Ludwigshafen, and certain other important works in Europe and America, to-day use diaphragms very successfully. At the present time 33,000 h.p. are used altogether in such works in various countries, with a total production of 70,000 tons of sodium hydroxide and 120,000 tons of bleaching powder.

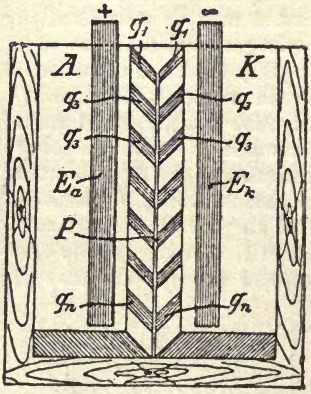


Fig. 222.

Of the numerous methods and forms of apparatus for decomposing sodium chloride solutions electrolytically with the employment of diaphragms, we shall record only the most important. Ordinarily the solution of the chloride is electrolysed at a temperature of 80° to 90° with a current of 100 to 200 amps. per square metre of electrode surface and at a tension of 3·5 to 4 volts.

After the greater difficulties encountered in the manufacture of resistant diaphragms had been overcome, these methods, which were those first attempted for the preparation of electrolytic caustic soda, regained the upper hand, and the consumption of electrodes and of diaphragms does not form such a serious item in this industry as in the past, when it prevented its development.

Most of these diaphragms, which act as osmotic membranes, offer great resistance to the passage of the current and do not even separate the products of the electrolytic dissociation very well.

The firm of Meister Lucius und Brüning of Höchst has partly overcome this difficulty by applying to the two sides of the diaphragm, *P* (Fig. 222), a series of non-porous bands, *q*, arranged in the same way as a Venetian blind, and inclined upwards, as shown in the figure, in such a manner that the bubbles of gas are forced to rise. In America diaphragms of sheet asbestos coated with cement have been used since 1903; these offer much less resistance to the current than other diaphragms.

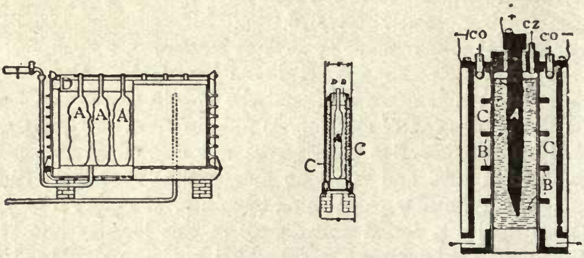


Fig. 223.

A process which has enjoyed much success during recent years and has been applied on a vast scale by an English company for the production of sodium carbonate and chloride of lime is that of Hargreaves in its latest modification (1898). The electrolytic cell is constructed with a diaphragm about 6 mm. thick, formed of an asbestos fabric impregnated with sodium silicate, and compressed into sheets, which allows osmotic phenomena, but not filtration of the liquid to occur. The external face of the diaphragm, *D* (Fig. 223), is connected with the cathode, *C*, formed of a close gauze of copper wire, or of a perforated plate. The internal portion between the two diaphragms forms the chamber in which the salt solution is placed, and the carbon anodes, *A*, dip into this solution. The cathode chamber does not contain any liquid, but a jet of steam or a spray of water is introduced in order to dissolve the sodium as fast as it is formed when the system is working. The sodium hydroxide solution collects at the base of this chamber, and if direct production of sodium carbonate is desired it is only necessary to pass in a current of moist carbon dioxide. The chlorine escapes from the anode chamber through a tube at the top.

Through special circumstances this process has acquired a certain importance in England. Each cell has a surface of 10 sq. metres of diaphragms and of cathodes, and decomposes 106 kilos of NaCl per twenty-four hours, producing 177 kilos of chloride of lime containing 37 per cent. of active chlorine, and 95 kilos of calcined soda containing 98 per cent. of Na_2CO_3; an electric current of 2300 amps. at 3·9 volts is required, and the current efficiency is 97 per cent. The diaphragms are 3 metres long and 1·5 metres wide, last more than a month, and cost about 5*s.* 6*d.* each. A plant composed of 250 of these electrolytic cells occupies a space of about 3500 sq. metres.

Another process which has been applied practically is that of Le Sueur (1898). The apparatus consists of an iron tank containing the bath, and anodes formed of iridio-platinum gauze; the diaphragms are horizontal and corrugated; the cathode is formed of iron gauze.

The *Outhenin-Chalandre* process is employed in various works, especially in those of the Swiss and Lyonese Company, "La Volta," at Chèvres, near Geneva, and at Montiers in Savoy, and those of the Società Elettrochimica of Bussi.

The apparatus is shown diagrammatically in Fig. 224. The box, *B*, is constructed of ebonite or cement and contains the anode, *c*; one side of it is furnished with a double wall, *C*, which does not reach to the bottom; the two opposite walls of this box are perforated by long, porous, inclined tubes open at the two ends, which serve as diaphragms, and contain the cathodes, *b*, formed of metallic plates united to the negative pole. The anode is placed between two series of these tubes; the whole is placed in a large tank, *A*, which contains a solution of alkali hydroxide, and the NaCl solution is passed into the ebonite tank through the upper tube. When the current passes chlorine is evolved through the tube *b*, whilst the sodium separated at the cathode inside the tubes is transformed into sodium hydroxide, a solution of which passes out through a syphon tube, whilst fresh water continuously passes in. The hydrogen evolved in the inclined tubes passes up these and collects in the chamber formed by the double walls, from which it passes into gasometers to be utilised.[1]

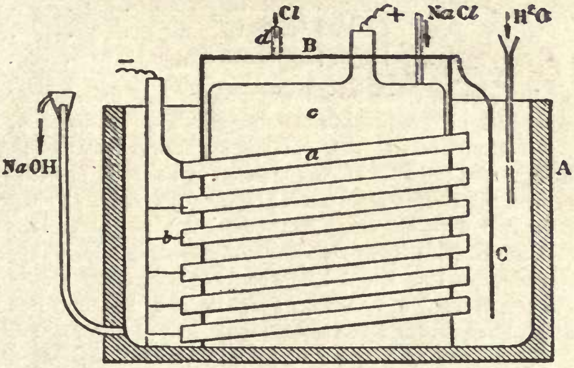


FIG. 224.

III. ELECTROLYSIS OF THE FUSED CHLORIDE. Lyte (1892–1895) endeavoured to decompose the fused lead chloride obtained as a by-product in various industries by means of the electric current. The idea of a process of decomposing molten chlorides by

---

[1] A well-designed diaphragm apparatus—applicable also to small plants—for the consumption on the spot of the caustic soda solution and the absorption of the chlorine by milk of lime and the direct utilisation also of the calcium hypochlorite solution (*e. g.*, in large bleaching works or for mercerising cotton or making cellulose), is that of Billiter, erected by Messrs. Siemens and Halske of Berlin. V. Engelhardt (1911) calculated the cost of the soda and chlorine used on the spot for a plant consuming 60 kw. (500 amps. at 120 volts) for the electrolysis and 12 kw. for mechanical purposes: Power during 8000 hours per year at 0·25*d.* per kw.-hour, 72 × 8000 × 0·25 = 144,000*d.* = £600; 250 tons of salt at 15*s.* per ton = £187 10*s.*; 200 tons of lime at £1 per ton = £200; 167 tons of coal at 18*s.* per ton = £150 6*s.*; six workmen at £60 per annum = £360; sinking fund (10 per cent.) and maintenance of £2400 worth of plant (£1400 for electrolytic baths, £105 for electrical connections, £312 for chlorine-absorption plant and tubing, £400 for evaporating plant for concentrating the soda solution to 35° Bé., £182 for various expenses); sinking fund (3 per cent.) on buildings and foundations to the value of £1600 = £48; interest on capital of £4000 = £200. The total is £1960 to produce 141 tons of NaOH (in solution) and 333 tons of calcium hypochlorite with 35 per cent. of active chlorine. The cost of the caustic soda may be calculated as £8 per ton, and that of the chloride of lime as £2 10*s.* per ton. If the power costs 0·625*d.* per kw.-hour, the total cost rises to about £2800 and the soda must be taken at £10 8*s.* per ton, and the chloride of lime at £4 per ton. If solid caustic soda (95 per cent.) is required, the consumption of coal for the concentration would be about 2 tons per ton of NaOH. With new Billiter plant, 9·30 kilos of Cl and 10·47 of NaOH are obtained per kw.-day.

a dry method was thus started. In the electrochemical works at Bitterfeld electrolytic soda is also prepared by a dry method, but the details are kept secret. In France the *Hulin* process was tried, but was abandoned because various difficulties were met with and a large quantity of electrical energy was required, the current efficiency being low. The process is based on the decomposition by the current of molten sodium chloride, contained in a large crucible. The crucible was placed in a furnace and large carbon anodes were used, molten lead being employed as the cathode. The latter combined with the sodium as it was formed, producing an alloy of lead with 25 per cent. of sodium, which was collected in the liquid state and decomposed with steam in separate vessels under proper precautions.

A current of 7500 amps. per square metre was used at a tension of 7 volts; 81 grms. of chlorine and 54 grms. of sodium were obtained per electrical h.p.-hour.

In Savoy, near Modano, trials were made of the *Vautin* method, which is a slight modification of the preceding one, but it was abandoned. An E.M.F. of 6 volts was required and a current of 7500 amps. per square metre; each horse-power produced 1·24 kilos of sodium and 1·85 kilos of chlorine daily.

In order to show the inferiority of this method compared with the wet methods, it is sufficient to note that to obtain 9 tons of sodium hydroxide (70 per cent. of Na_2O) the following amounts of electrical energy are required:

By the Hargreaves-Bird process . . .	2609 kw.-hours
„ Castner-Kellner „ . . .	2694 „
„ Hulin (dry-method) „ . . .	6106 „

In order to work by the dry process it is therefore necessary to have at disposal large quantities of cheap electrical energy. This condition is realised at Niagara Falls, where the *Acker* process (1900), which is an improvement of the preceding process, is used. By this process the heat of combination of the sodium with steam is utilised, the hydrogen so formed being also employed for heating purposes. This process still consumes much energy compared with the other methods, but a ten times larger production of soda is attained and the sodium hydroxide thus obtained at high temperatures is free from water. The consumption of electrodes, especially of the cathodes, is, however, very large, although these are constructed of Acheson graphite and last one hundred times longer than those of amorphous carbon; the latter are destroyed in a few minutes.

CONCENTRATION OF THE CAUSTIC SODA SOLUTIONS. The solutions are evaporated in well-polished iron pans, to a density of 38° Bé.; the impurities, consisting of Na_2SO_4 and Na_2CO_3, then settle. The decanted liquid is evaporated at 360°, and when almost all the water has thus been driven off small portions of nitre are added or air is passed through in order to oxidise the cyanogen compounds and sodium sulphide which are present as impurities.

The pure molten sodium hydroxide is then poured into iron or nickel drums, which are hermetically sealed, and after cooling are ready for transport. Each drum contains 150 to 200 kilos of NaOH. Complete evaporation from 38° Bé. requires about 100 kilos of coal per 100 kilos of NaOH, and it is on this account that the concentrated solutions (38° to 40° Bé.) are, if possible, sold directly, especially where the consumer is not far away. In addition to saving of coal to the manufacturer, the consumer is spared the trouble of breaking up and dissolving the solid caustic soda. For many industries, especially for soap-making, the use of solutions ready made is of advantage, but for other organic industries in which fusions with caustic soda are carried out, the use of solid soda is indispensable.

In order to economise fuel in the preparation of solid sodium hydroxide, ingenious vacuum evaporating plants have been introduced; these are also extremely suitable for the economical concentration of saline solutions, even of such very dilute solutions (2° to 3° Bé.) as are obtained on washing mercerised cotton fabrics in order to remove the concentrated NaOH solution. It is thus possible advantageously to recover sodium hydroxide which would otherwise be lost.

These forms of apparatus were at first especially applied in the sugar industry, but their use has now spread to many other industries. They are based on the principle that liquids boil at lower temperatures when exposed to less than atmospheric pressure.

The simple vacuum plants have now almost ceased to exist, and are replaced by multiple-effect evaporators, in which the steam developed in a first closed evacuated boiler, enters a coil immersed in the liquor in a second boiler maintained at a lower pressure than the first, so that the vapour from the first boiler causes the liquid in the second to boil, and the steam evolved in the second boiler causes the liquid in a third boiler at still lower pressure to boil, and so on. In Vol. II., "Organic Chemistry," in the section on Sugar, the theory of vacuum concentrating pans is explained and illustrated by various practical forms of plant.

Later, in the section on Sodium Chloride, we illustrate a triple-effect evaporator, and we shall here describe a new form of plant with a sextuple effect—the Kestner plant (Fig. 225).

The six tubes which are seen in the figure act as evaporating boilers. They are 7 metres high, and connect at the top with a spherical chamber which acts as a steam separator. When in work the apparatus contains 500 litres of moving liquid in place of 15,000 litres contained in an ordinary quadruple-effect evaporator. The saline solution is concentrated in a single passage through the apparatus, lasting only a few minutes. The influx of the liquor into the first boiler regulates the concentration at the exit of the apparatus.

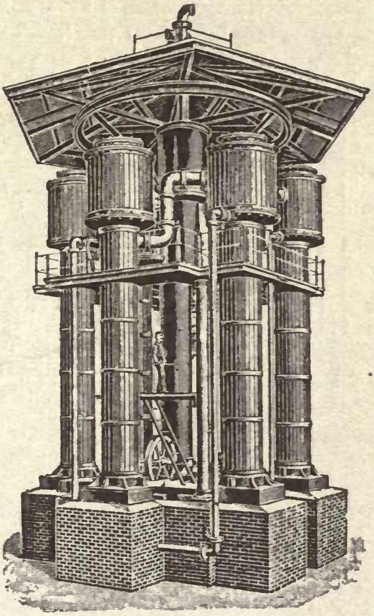


FIG. 225.

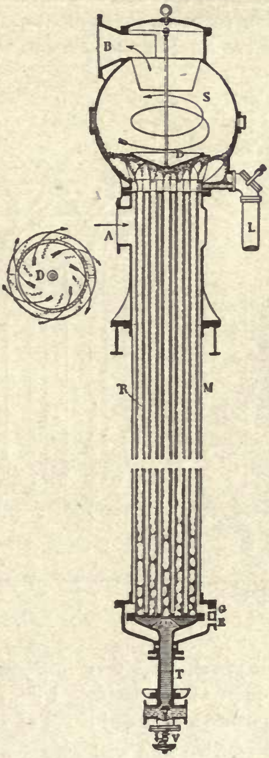


FIG. 226.

Fig. 226 represents a section of an element of the plant shown in the preceding figure; each element consists essentially of a bundle of evaporating tubes and of a spherical steam separator.

(*a*) The bundle of evaporating tubes is formed of tubes, *R*, of 5 to 7 or more metres in length, placed in a steam chamber, *M*. All the tubes communicate below with a chamber fed by a single tube, *T*, which enters the base of the steam chamber through a stuffing-box. All the tubes are screwed into a perforated plate on which the separator is mounted. This arrangement allows the bundle of tubes to expand absolutely freely. The steam passes in at *A*, the condensed water is discharged at *E*, and the steam and air pass off at *G*.

(*b*) The separator, *S*, is of spherical shape and comparatively small volume; it encloses an apparatus, *D*, which carries wings similar to those of a centrifugal pump. The apparatus, *D*, is closed, and the form of its wings is such that the vapours which collide with them acquire a rotary movement in the separator indicated by the arrow. This rotary movement causes the liquid carried over with the steam to separate from it, through the action of centrifugal force. The condensed liquid is discharged at *L* and the vapour formed in the bundle of tubes escapes at *B*.

The liquid to be concentrated is fed in continuously through the tube *T*, and enters equally all the tubes which form the bundle. The ebullition (due to the steam in the chamber surrounding the tubes) produces first bubbles and then steam in each tube, increasing in volume and in velocity. This carries the liquid up to form a thin layer which adheres to the wall of the tube, causing inside the tubes a phenomenon which Kestner calls "*grimpage*," and which is indicated graphically in Fig. 226. At the top of the tubes the liquid has a velocity of 20 to 25 metres per second, and is thrown against the throttle, *D*, which causes the mixed steam and liquid to acquire a rotary movement, so that dry steam escapes through *B* and passes to the next unit of the apparatus or to the condenser.

When these Kestner plants are applied for the concentration of very dilute solutions, such as the liquids recovered in the mercerisation of cotton fibres and tissues (*see* Vol. II., "Organic Chemistry," section on Textile Fibres), which have a concentration of about 2° Bé., the concentration is usually carried to 12° Bé. in the first elements of the apparatus; the solution is then passed into the boiler, *C*, as is seen in the general diagram in Fig. 227, and milk of lime is here added in order to causticise the sodium carbonate formed by continuous contact with air during the process. After boiling for one hour the hot solution is then passed through a filter-press in which the milk of lime and calcium carbonate are retained by close cotton fabrics, and the clear solution is then concentrated in the final elements to the required density of 32° to 38° Bé.

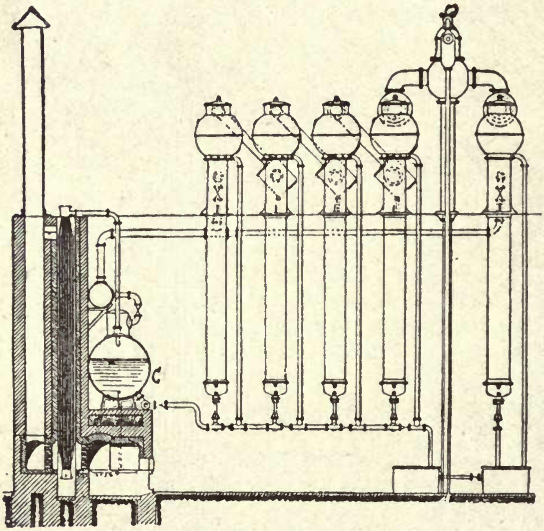


FIG. 227.

To show the very great economy of fuel which is attained by such plant, we give a few comparative figures.

In order to concentrate 1 cu. metre of NaOH lye from 10° to 48° Bé., that is, in order to evaporate about 850 litres of water, there are required by direct firing 222 kilos of coal.

By indirect heating with steam without vacuum	181	„
„ „ „ with vacuum and single effect . .	117	„
„ „ „ „ „ double „ . .	59	„
„ „ „ „ „ triple „ . .	41	„
„ „ „ (Kestner) with sextuple „ . .	22	„

In plant with quadruple effect each kilo evaporates up to 35 kilos of water.

APPLICATIONS, PRICES, AND STATISTICS.[1] Caustic soda is used in large quantities in the manufacture of soap, which consists of the potassium or sodium salts of

---

[1] A works for the daily production of 3·15 tons of sodium hydroxide and 7·5 tons of chloride of lime would cost (prior to the European War) about £12,000 for plant, exclusive of plant for motive power and steam production. The complete daily cost of working would be £54 and the gross daily profit about £69. We give in detail the expenses which would be incurred in England, but they would have to be altered considerably to suit Italian conditions.

The daily expenses in an English works may be estimated as follows: 5·85 tons of salt, £3 8*s.*; 4·53 tons of lime for absorbing the chlorine, £5 5*s.* 7*d.*; 0·9 ton of hydrochloric acid, £4 4*s.*; 7 tons of coal for evaporating the sodium hydroxide solution and producing a portion of the power (250 h.p.), £4 8*s.*; the wages of 45 people at a mean daily wage of 6*s.* 9*d.* = £15 4*s.*; administration expenses, £1 12*s.*; packing, £3 4*s.*; lubricants, various stores, and losses, £2 2*s.* 5*d.*; rates and taxes and insurance, £1 1*s.* 8*d.*; repairs and sinking fund, £5 5*s.* 7*d.*; various expenses, £1 1*s.* 7*d.*; daily charge for 1000 electric h.p. at £2 11*s.* per h.p.-year, £7. The gross daily profits from 9 tons of chloride of lime at £5 per ton would be £45, and for 3·15 tons of sodium hydroxide at £10 per ton, £31 10*s.*, from which one must deduct £11 12*s.* for freight.

fatty acids. Caustic soda is also used in paper-mills, cotton-mills, aniline dyestuff factories (for the preparation of alizarin, resorcinol, naphthol, etc.), for mercerising cotton (*see* Vol. II., "Organic Chemistry," section on Textile Fibres), for purifying petroleum, mineral oils, etc.

Caustic soda is sold in concentrated solutions the strength of which is indicated by its degrees Bé., or, better, by the percentage of NaOH. More commonly, however, it is sold in the solid state, and the content of Na_2O is then given, 100 per cent. NaOH containing 77·5 per cent. Na_2O; the two qualities of solid caustic soda sold contain 72 to 74 per cent. and 75 to 77 per cent. Na_2O.

The production of sodium hydroxide is carried out more especially in England and in Germany; the latter country produced 70,000 tons of caustic soda in 1901, of which only 5000 tons were electrolytic (now much more), and 35,000 tons of potassium hydroxide, of which 30,000 tons were manufactured by the electrolytic process. Germany exported about 6000 tons of caustic soda in 1905, of the value of £60,760, 8340 tons in 1909, and 13,000 tons (also 44,112 tons of KOH) in 1913.

France exported 14,144 tons of caustic soda in 1913, 8792 tons in 1914, and 396 tons in 1915; the production in 1913 amounted to 80,000 tons (14,000 exported), only partly electrolytic. England exported 79,000 tons in 1909, 83,000 in 1910, and 81,000 in 1911, produced almost exclusively by the United Alkali Company; in 1914 this powerful company reduced its capital from £3,000,000 to £600,000, its decline being due to the rapid diminution of the exports to various countries, which began to produce for themselves and protected their industry with high Customs' duties. The competition was also aggravated by the Solvay works, which in these countries produced caustic soda, both electrolytically and from the carbonate, by causticising with lime.

In Russia the consumption of caustic soda in 1897 was 23,500 tons, of which 7770 tons were imported from Germany and from England; in 1907 the consumption rose to 38,336 tons, and the imports fell to 208 tons, while the production reached 42,000 tons in 1909 and 47,600 in 1910, when all importation ceased.

Spain imported caustic soda to the value of £80,000 in 1909 and £39,400 in 1910. In Belgium 2000 tons were made in 1912. The imports to Brazil were valued at £96,000, and those to the Argentine amounted to 5990 tons in 1910 and to 5515 tons in 1911.

In Italy the production of electrolytic caustic soda was started in 1903 in the Bussi (Aquila) works of the Italian Electrochemical Company of Rome, in 1906 in the Brescia works of the Caffaro Electrochemical Company—where the product is almost exclusively caustic soda solutions of 38° Bé., as they come from the electrolytic baths—and in 1916 at the Vitali Works at Rumianca (Novara) (capacity 10 tons of solid NaOH per day). The last-named and also the Caffaro Company use Solvay electrolysers with mercury cathodes, whilst at Bussi use is made of electrolysers with Outhenin-Chalandre diaphragms of cement and anodes of magnetite.

The caustic soda produced in Italy and that imported are shown in the following table:

	Solid caustic soda (Bussi) Tons	Solution at 38° Bé = 32·5° (Brescia)	Total output as NaOH	Imports, solid
1903 . .	2500	—	2375	16,504
1905 . .	2200	—	2190	—
1906 . .	1500	1700	2000	15,750
1908 . .	2715	4196	4000	14,290
1910 . .	3078	5400	4725	15,883
1911 . .	3341	5200	4920	14,894
1912 . .	4039	6715	6100	16,707
1913 . .	3470	6877	5600	16,375
1914 . .	3282	7661	5700	15,191
1915 . .	3289	8300	6000	21,480
1916 . .	4500 (approx. with Rumianca)	—	—	19,844
1917 . .	—	—	—	17,847

In spite of this increase in the Italian output, importation has not yet been eliminated, since the output is limited by the excessive amounts of chlorine and chloride of lime (with every ton of caustic soda there corresponds more than 2·5 tons of chloride of lime), which find no outlet in Italy.

Before the European War, the price of solid caustic soda varied from £10 to £13 per ton, according to the strength and purity; solutions of 38° Bé. (= 32 per cent. NaOH) were sold at £4 to £4 8*s.* per ton.[1] During the war the price of the solid rose to more than £120 per ton.

SODIUM CHLORIDE : NaCl (Common Salt)

This salt is the raw material for the preparation of almost all the other artificial sodium salts. It is widely diffused in nature, and is found abundantly in sea water (about 3 per cent.), from which it is extracted industrially in France, Italy, and other countries. It is found in very important tertiary deposits as *rock-salt*, and abounds in Wielezka in Poland, in Austria, Spain, England, and Roumania, but more especially at Stassfurt, where there are immense deposits which extend over kilometres of surface and have a thickness at certain points of 500, 900, and even 1500 metres. It is also found in moderate quantities in Sicily.

We have discussed the manner in which these immense deposits were formed, in connection with Stassfurt salts (*see* p. 530), and we still see similar deposits being continuously formed to-day in the regions south of the Dead Sea, which contains up to 8 per cent. of NaCl (*see* Analysis, p. 228).

When these are pure it is obtained directly from the large rock-salt deposits by the ordinary methods of mineral mining, that is, by excavating galleries and carrying the salt to the surface in blocks.

If the rock-salt deposits are at a great depth (1000 to 2000 metres) or if

---

[1] **Analysis of sodium hydroxide.** In order to determine the commercial value of a consignment of caustic soda it is necessary to take great care in the selection of the sample by removing several pieces from various parts of the molten block immediately after the vessel containing it has been opened and the block broken up. The pieces, amounting altogether to at least a kilo, are immediately placed in a dry glass vessel closed with a good stopper of glass or of paraffin-waxed cork, so that they may not absorb moisture and carbon dioxide from the air.

The larger pieces are rapidly broken up before analysis and about 20 grms. are placed in a weighing-bottle with a ground-glass stopper. This is carefully weighed, and the contents are poured into a graduated litre flask and the caustic soda dissolved in freshly boiled distilled water, the weighing-bottle being reweighed; from this solution various portions are taken for the determination of impurities (sulphates, chloride, etc.) and of the strength in sodium hydroxide and sodium carbonate, exactly as is indicated below for the analysis of sodium carbonate; thus 20 c.c. of the solution may be titrated almost at the boil with $\frac{N}{2}$ hydrochloric acid in presence of litmus as an indicator; 1 c.c. of $\frac{N}{2}$ acid corresponds with 0·02 grm. of NaOH or 0·0265 grm. of Na_2CO_3. This first result gives the total alkalinity, which for the moment may be calculated as Na_2CO_3; 20 c.c. of the solution of caustic soda are then treated with an excess of barium chloride solution (5 c.c. of 10 per cent. solution) and the volume made up to 100 c.c. with water; the carbonate which is always present in greater or less amount in caustic soda is thus precipitated and sodium hydroxide alone remains in solution; 50 c.c. of the clear solution are removed and titrated with $\frac{N}{2}$ acid in presence of methyl orange or phenolphthalein; by calculating this second result as NaOH we have the content of true sodium hydroxide. By calculating this as sodium carbonate and subtracting it from the total alkalinity found by the preceding test, the quantity of sodium carbonate contained in the sample is found.

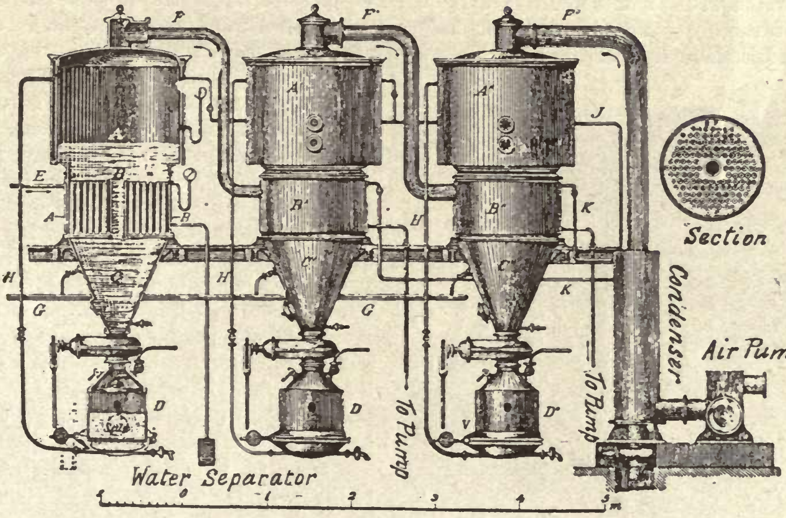
The quantities found in 20 c.c. of solution are re-calculated into weights per 100 grms. of the sample under examination.

The strength is ordinarily expressed in English degrees, that is, in percentages of Na_2O; the German, Newcastle, and Descroizilles degrees will be explained below in connection with the analysis of sodium carbonate.

The water is determined by difference, because direct determinations by heating in an oven are not exact, and it is more accurate to determine the carbonate, hydroxide, iron, alumina, sulphates and chlorides, the rest being water. The composition of a commercial caustic soda manufactured by the firm of Solvay of 76° to 77° strength was as follows : $Na_2O = 76·1$ per cent. (= 95·203 per cent. of NaOH), $Na_2CO_3 = 1·82$ per cent., $Al_2O_3 + Fe_2O_3 = 0·017$ per cent., $NaCl = 1·93$ per cent., $SO_4Na_2 = 0·48$ per cent., water 0·55 per cent.

the salt is impure, that is, mixed with earth, gypsum, etc., the sodium chloride is extracted by water, by drilling wells and removing the saturated solution, which is then evaporated in order to recover the crystallised salt.

In the hot countries of the Mediterranean basin, salt is extracted from sea water, which is evaporated by means of the sun's heat in a series of very large flat basins excavated in the earth and communicating with one another, the so-called *salt-pans.* The water enters the first basins at high tide, and in these the less soluble impurities and suspended matter (gypsum, clay, calcium carbonate, iron, etc.) are deposited. It then passes into the so-called concentrating pans, where it is partially evaporated (up to 30° Bé.), and deposits pure crystallised salt. The remaining solution is concentrated in successive basins, where a mixture of sodium chloride and magnesium sulphate is deposited, and finally from the last mother-liquors, a further mixture of potassium chloride, magnesium chloride, and varying quantities of potassium bromide and iodide is obtained (*see* p. 530). These salt-pans sometimes occupy an area of thousands of acres. The Silician salt-pans yield three to five complete crystallisations per annum, and produce 220,000 tons in all, without including twenty rock-salt mines.



The section shown is at *AB*.

FIG. 228.

In cold countries sea water is allowed to freeze in winter, by which means ice almost free from salt is separated, and this operation is repeated until a concentrated solution is obtained, this being then evaporated over direct flame in large pans, or, as at Stassfurt, evaporated in Pick triple-effect vacuum pans, based on the principle of Rillieux and of Robert (*see also* Sextuple-Effect Apparatus, p. 563, *and* Vol. II., "Organic Chemistry," section on Sugar): the salt solution enters the first boiler (Fig. 228), where its boiling-point is lowered by diminishing the pressure by means of a pump, and on heating by a bundle of tubes, *B*, in which circulates steam coming from the boiler through the tube *E*, evaporation takes place; the steam which escapes from the first boiler, *A*, has a temperature below 100°, and, passing through the tube *F*, heats the solution contained in the second boiler, *A'*, where the pressure is still less than in *A*, so that this liquid boils at a still lower temperature; the vapours which escape from *F'* and which have again a still lower temperature serve to boil the salt solution in the third boiler, *A''*, in which a still higher vacuum is produced by the pump and by condensing the vapours from *F''* by means of a jet of water. The solution enters the boilers through the tube *G*, and as the salt gradually crystallises it passes into vessels, *D*, which are provided with a perforated false bottom which retains the salt whilst the mother-liquor returns to the boiler through the tube *H*. Every two or three hours the salt is discharged from the chamber, *D*. At the boiling-point the salt separates in fine crystals, whereas if it crystallises from the mother-liquors at 50° to 60° larger crystals separate and at 45° to 50° crystals and large incrustations. A small Pick apparatus may produce one ton of salt per twenty-four hours. It must, however, be noted that in these and other forms of apparatus for concentrating saline solutions, serious trouble is caused by the incrustations of calcium sulphate produced by the gypsum dissolved in the salt water—this separates before the NaCl—and by the separation of NaCl crystals. In 1898 Vis patented a process for avoiding this difficulty by effecting separation of the gypsum from the brine by the addition of $CaCl_2$ or Na_2SO_4, that is, of two very soluble salts which cause a concentration of Ca or SO_4 ions, and therefore separation of the calcium sulphate (pp. 96 and 542). Sometimes milk of lime is simply added in amount just sufficient to precipitate salts of magnesium.

M. Monsanto recommends addition of trisodium phosphate to precipitate the gypsum. Further, short electrolysis produces a little NaOH, which precipitates calcium sulphates and bicarbonates (*see* p. 242). In any case the solutions are filtered before vacuum concentration. G. Emilio (Ger. Pat. 200,199, 1907) evaporates the salt solutions to dryness by passing them on to a revolving cylinder with a fixed furnace inside; at 140° to 160° the evaporation of the film of liquid is rapid, and the separated salt is scraped from the surface of the revolving cylinder by means of a knife; the steam generated is collected and led under the tanks holding the salt solution. The moist salt holding mother-liquor obtained from the concentration apparatus is centrifuged or dried in pans, in which it is kept stirred to prevent the formation of hard crusts.

In certain parts of Germany saline solutions are concentrated by so-called *gradation*, which consists in repeatedly pumping the salt water to the top of a framework 10 metres or more high (Fig. 229), filled with bundles of thin twigs. The solution falls from the top in a finely divided shower, passing over a large evaporating surface formed by the wooden twigs. Evaporation is helped by the sun and wind, but much salt (20 to 30 per cent.) is lost by passing away into the air. When the liquid has acquired a certain concentration it is finally evaporated in boilers or preferably in Pick vacuum pans. During wintry weather, or when the wind is too strong, this method does not work. It is being abandoned more and more, as it is more convenient to saturate the solutions with rock-salt which has been purchased, but in some districts it is continued, since air rich in salt, as at the sea-shore, is required in neighbouring sanatoria.

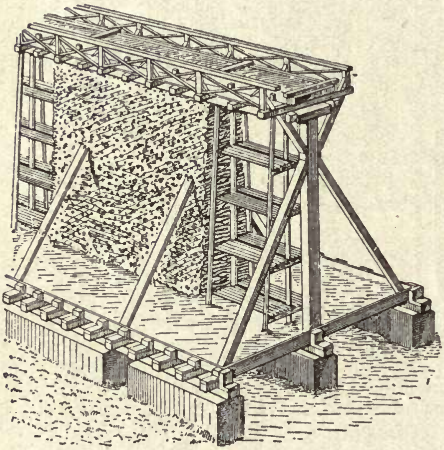


FIG. 229.

In 1895 Hirsel proposed the separation of salt from concentrated solutions by cooling them to − 10° or − 20°, so causing almost complete crystallisation of the salt as NaCl, $2H_2O$, which is then dehydrated.[1]

---

[1] **Kayser's Process for the Evaporation of Saturated Solutions of Rock Salt.** It is known that when steam at 100° is passed through a salt solution, the latter is brought to a temperature above 100°, as it has a vapour pressure less than 1 atmos. at 100°; the rise of temperature is given by the heat of condensation of the steam (*see* pp. 85, 225). In about 1888 Honigmann heated to boiling a locomotive boiler containing concentrated caustic soda solution, the steam developed, after being made to work a steam engine, being passed into the boiler to keep it boiling; thus, the intermediate locomotive works without a fire. The same principle was utilised later by Kayser with concentrated calcium chloride solution, but to evaporate saline solutions. In either case it is necessary to furnish the heat to reconcentrate the salt solution which is diluted by the steam, but from this, Kayser asserts, steam can be obtained at a higher pressure than is given by these solutions on simple concentration in the ordinary way. Kayser considers the working of the following arrangement: In a saturated solution of sodium chloride heated to boiling (109°) is immersed a coil through which circulates saturated calcium chloride solution at 140°; the steam from the NaCl solution is condensed in a Honigmann condenser by means of a fine spray of the calcium chloride solution which has already passed through

PROPERTIES. Sodium chloride crystallises in transparent cubes of sp. gr. 2·13, which sometimes form hollow quadratic pyramids formed of little steps. Its solubility is almost the same in hot or cold water; thus at ordinary temperatures 26 per cent. is dissolved, and at 100° 28 per cent. The saturated solution deposits at −10° large monoclinic tablets of $NaCl + 2H_2O$, which lose water at 0°, and are then transformed into cubes. The degrees Bé. indicated by hydrometers immersed in salt solutions also indicate the percentage of salt directly. It melts at 815°, boils at 1750°, and evaporates at a white heat. When heated, salt decrepitates, owing to evaporation of the interstitial water enclosed by the small crystals. Salt allows of the passage of 92 per cent. of the heat rays (glass only 24 per cent., ice zero).

The bluish reflection and colour exhibited by certain deposits of rock-salt are due to the presence of traces of colloidal metallic sodium.

The composition of *cooking salt* varies between the following limits: 88 to 99·7 per cent. NaCl, 0 to 0·2 per cent. KCl, 0·1 to 2·8 per cent. $MgCl_2$, 0·2 to 0·6 per cent. $CaCl_2$, 0·2 to 3·5 per cent. $MgSO_4$, 0·2 to 1·9 per cent. $CaSO_4$, 0 to 1·2 per cent. Na_2SO_4, 0·4 to 0·6 per cent. K_2SO_4, 0·4 to 1 per cent. of insoluble matter, and 0·6 to 8 per cent. of moisture. The magnesium chloride more especially renders salt deliquescent.

USES OF SALT. As well as for seasoning food and preserving it (meat, vegetables, fish, etc.), salt is used in the manufacture of various important chemical products: sodium carbonate and hydroxide, chlorine, aniline colouring matters, soaps, glasses, ceramic products, chlorates, hypochlorites, hydrochloric acid and sodium sulphate and bisulphate, and also for preparing brine for ice machines (*see later:* Calcium Chloride).

STATISTICS. The world's output of salt in 1909 to 1910 reached 18,000,000 tons, distributed thus: Germany, 2,094,023; Russia, 1,879,717; England, 1,851,908; France, 1,113,061; Spain, 836,708; Austria-Hungary, 755,000; Portugal, 200,000; Belgium, 100,000; Switzerland, 57,622; Turkey, 265,114; Roumania, 129,287; Greece, 23,988; Bulgaria, 16,000; British India, 1,300,500; China, 1,700,000; Japan, 622,289; Algeria and Tunis, 44,000; United States, 3,850,182; Canada, 81,260.

From the consumption of salt in various countries the degree of industrial development and of civilisation of the inhabitants may be deduced; thus the more civilised nations have greatly reduced or abolished the State monopoly of this product, which is a prime necessity for the people.[1]

---

the coil and is partly cooled. In contact with this steam the calcium chloride solution should, according to Kayser, resume the temperature of 140° and so become ready to pass again through the coil and evaporate fresh calcium chloride solution, and so on.

Kayser's conclusions have been adversely criticised by Jänecke and his process has been received with diffidence. The only plant erected—at Lubeck in 1913—cost £12,000 and was to deal with 9000 tons of salt per annum. It worked spasmodically until 1914 with a consumption of 25 kilos of coal per 100 kilos of salt, but to concentrate the dilute $CaCl_2$ solutions it was necessary to introduce a triple effect apparatus. In Germany Kayser was not granted a patent for his process, which, for various reasons, failed in practice.

[1] The following table shows the production and consumption of salt in various countries, the difference between the consumption and production being due to that used in industries or for exportation or importation. A further column shows the mean annual consumption per inhabitant, including the salt used for both industrial and alimentary purposes. The figures refer to 1896, but are little different to-day, in so far as they refer to alimentary salt; for Italy, this amounted, indeed, to 6·9 kilos per inhabitant.

These figures are disconcerting from the Italian point of view, because they place Italy almost at the tail of civilised nations, salt being not only a condiment for the gourmet, but a substance indispensable for the proper assimilation of food, because it is necessary for the production of the hydrochloric acid of the gastric juice; each healthy individual therefore requires at least 8 kilos of salt per annum merely for the performance of normal physiological functions.

It must also be remembered that the pre-eminently carnivorous populations of England, Belgium, and France already obtain a portion of the salt which they require in the meat which they eat, whilst the Italians, and especially the inhabitants of the open country, are mainly vegetarians, and should, therefore, consume larger quantities of salt than the inhabitants of other

The production of salt in Italy is as follows :

1871.	Sea salt	267,000 tons	Rock salt and spring salt	35,000 tons.
1902.	,, ,,	423,000 ,,	,, ,, ,, ,,	55,797 ,,
1910.	,, ,,	447,440 ,,	,, ,, ,, ,, ,,	61,014 ,,
1911.	,, ,,	460,439 ,,	,, ,, ,, ,, ,,	58,729 ,,
1912.	,, ,,	466,220 ,,	,, ,, ,, ,, ,,	59,050 ,,
1913.	,, ,,	585,028 ,,	,, ,, ,, ,, ,,	60,111 ,,
1914.	,, ,,	512,992 ,,	,, ,, ,, ,, ,,	33,267 ,,
1915.	,, ,,	382,156 ,,	Rock salt	17,914 ,,
1916.	,, ,,	330,000 ,,	Spring salt	67,237 ,,

The *price* of salt for domestic purposes in Italy was 2·88*d.* per kilo in 1848, 5·28*d.* after 1869, 3·36*d.* after 1884, and since 1894 3·84*d.* for granular salt, 5·76*d.* for ground salt and 7·68*d.* for refined salt in packets.

The cost of production in the Government salt works in 1914 was : 7·04*s.* per ton (9·76*s.* in 1910) for common salt, 17·92*s.* for ground salt, 64·88*s.* for refined salt, 25·12*s.* for agricultural salt, and 25·44*s.* (or 32*s.*) for industrial salt.

Italy exported a total of 85,500 tons of salt in 1908, 119,173 tons in 1911, 161,118 tons in 1913 at 56*s.* per ton, 108,991 tons in 1915, and 31,135 tons in 1916, the export being mainly from Sardinia and Sicily and, in 1913, to : Norway 71,179 tons, The Netherlands 20,797, the United States 12,902, Sweden 5421, etc.

The consumption of industrial salt in Italy in 1904 was distributed thus : 16,514 tons for the soda industry and for reduction of metals (denatured Sicilian salt, free from tax), 6114 tons for various industries (denatured), 7708 tons for agricultural uses, 3631 tons for refrigerating industries, 470 tons for salting fish, and about 5000 tons (?) for the soap industry (denatured).

Denatured salt is sold by the Government in Italy at cost price ; the denaturing agents vary with the use to which the salt is to be put, and include sodium bisulphate and lampblack (alkali manufacture), calcium hypochlorite and naphthalene (sodium hypochlorite manufacture), ferrous sulphate and potassium ferrocyanide, magnesium sulphate and phenol, etc., etc.

In 1904 Germany produced 1,080,000 tons of rock-salt, valued at £250,000 and 621,800 tons of sea-salt, of the value of £720,000. In 1908 Germany produced 1,332,000 tons of rock-salt, valued at £280,000 (in 1909, 1,371,000 tons and in 1912, 1,350,000) and 665,600 tons of cooking salt, of the value of £880,000, obtained from solutions or saline springs (in 1912,

---

countries. Since the exact opposite is the case, that which could reasonably be expected happens, and explains the sad pre-eminence of Italy in those who suffer from pellagra.

	Total production in tons	Total consumption in tons	Annual consumption per inhabitant in kilos			Sale price of edible salt per kilo
			Total	For industrial purposes	For alimentary purposes	
	1896	1896	1896	1896	1896	Pence
England and Ireland	2,146,850	1,656,500	43·7	31·2	12·5	1·06
Belgium	100,000	202,700	34·0	—	—	—
United States of America	1,261,600	1,497,700	23·8	8·8	15·0	—
France	842,500	809,500	21·5	16·3	5·2	2·40
Germany	1,049,640	871,140	17·6	9·9	7·7	2·40
Switzerland	40,000	48,000	16·4	—	—	1·92
Russia	1,392,000	1,392,000	12·3	4·0	8·3	0·96
Austria-Hungary	467,240	478,600	11·5	3·7	7·8	—
Italy	451,800	192,412	7·1	0·7	6·4	3·84
Spain	320,900	158,100	9·0	—	—	2·11
China	1,648,000	1,800,000	5·0	—	—	—
Total for the whole earth	13,241,800	13,241,800	8·9	—	—	—

650,000 tons).[1] France possesses rock-salt deposits 10 to 70 metres thick, which occupy an area of 400 sq. kilometres. In 1908 France produced 143,000 tons of rock-salt and 593,000 tons of salt from saline springs; in 1913, 141,626 tons of sea-salt and 32,889 of rock-salt were exported from France, in 1914, 94,231 and 14,189 tons respectively, and in 1915, 24,463 and 1783 tons respectively.[2] In 1904 Spain exported 350,000 tons of salt at 5*s.* 5*d* per ton (300,000 tons being sea-salt, of which three-fourths were produced at Cadiz). The output in other countries is shown in the footnote.[3]

SODIUM BROMIDE and IODIDE : $NaBr$ and NaI. The former melts at 760° and the latter at 690°. The bromide is slightly soluble in alcohol, the iodide very soluble. At

---

[1] In Germany the industrial salt used was distributed as follows :

	1908	1913
Total (four-fifths rock-salt)	956,436	1,112,806
Cattle salt	115,418	128,800
For soda and crystallised sodium sulphate	530,000	524,700
For dyes and chemical products	123,650	265,660
For tanning	14,200	15,257
For salting fresh hides	45,200	55,887
For metallurgical uses	22,100	35,312
For ceramic industry	9,100	11,680
For soap-making and oil-refining	14,720	14,798
For paper works	1,830	1,726
For textile industries	4,637	9,696
For ice-making and cold storage	11,000	12,956
For removing ice from tramways	8,100	4,426

Large quantities of saturated salt solution are also consumed.

For food, as cooking salt, 500,220 tons were consumed in 1909 and 524,309 in 1913. The German Government received £1,575,000 as salt tax in 1913, all cooking salt paying 1·44*d.* per kilo. The salt is sold retail at 2·88*d.* per kilo.

[2] In the department of Meurthe-et-Moselle (France) there were in 1905 twenty-two works for extracting salt from rock-salt deposits by means of borings 120 metres deep. When the salt solution is not used directly in chemical works, it is evaporated by allowing it to drop as a fine spray from the top of a brick tower up which passes hot air (*e. g.*, filtered flue gases); the dry salt reaches the bottom ready powdered (Cantenot process). In the south-eastern salt works 679,864 tons were obtained in 1905. The works on the Mediterranean coast are of some importance and those of Peccais (Gard) have an area of 2500 hectares, with an output of 17 tons per hectare (more than double this amount can be produced, and in windy regions of Corsica as much as 174 tons per hectare are obtained).

[3] In Austria salt is a Government monopoly and is found in the Alpine and Carpathian regions. The brine from the borings at Salzberg contains 304·76 kilos of $NaCl$ and 30·96 of other salts per cu. metre and is carried through pipes 37 kilometres in length to the Ischl and Ebensee evaporating works and to the Ebensee soda factory. The mine at Dürnberg (Salzberg) was known in the year 15 B.C., and after a long interval extraction was resumed in 1094 and is now in full activity. To reach the rock-salt borings must traverse 1850 metres of limestone. The great mine at Ebensee dates from 1607, and there are now large open evaporating pans there with an area of 2182 sq. metres, and the heating is effected by means of 64 furnaces with inclined hearths; in 1906, 204,276 cu. metres of brine (with 301 kilos of salt per cu. metre) were evaporated and 60,751 tons of salt obtained. The Hall mine in the Tyrol dates from the year 837, and in 1906 produced 16210 tons of salt in six evaporators. In the Carpathians the Drohobycz mine (Galicia) dates from 1340, and evaporation is now carried out with petroleum residues as fuel. The mines of Eastern Galicia yielded 58,508 tons of salt in 1906, but the largest rock-salt deposits are found in Western Galicia at Wieliczka and Bochnia. At Wieliczka three qualities of salt are obtained: the Szybiker salt, with 98·3 per cent. $NaCl$, the Spiza salt with 94·5 per cent. $NaCl$, and the green salt with 96 per cent. $NaCl$; the total output was 94,316 tons in 1906, and at Bochnia 23,728 tons. Salt is also found in Istria and Dalmatia.

The output of salt in the United States in 1910 was 3,849,830 tons (3,823,671 in 1909), classified as follows: table salt, 444,370 tons; fine ordinary salt, 781,468; granulated ordinary salt, 330,547; solar salt, 155,368; rock-salt, 884,674; salt in solution, 1,193,432 tons. The imports were 143,000 tons in 1910 and 138,000 (£75,600) in 1911.

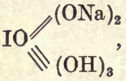
In Great Britain the largest rock-salt centre is in Cheshire, where the deposits are as thick as 31 metres and the output reaches 100,000 tons per annum. A much larger quantity of salt is, however, obtained from natural salt solutions, these containing 25·32 per cent. $NaCl$ and 2·1 per cent. of other salts, and yielding about 1,600,000 tons yearly. The British output of salt was 2,778,897 tons in 1877, 2,229,164 in 1887, 1,934,944 in 1897, 2,016,510 in 1907, 2,050,630 (£581,600) in 1910, 2,247,758 in 1913, and 2,069,989 in 1914; the exports amounted to 515,443 tons in 1909, 562,812 in 1910, and 604,864 (£487,200) in 1911.

Russia produced 2,485,000 tons of salt in 1909 and 1,966,000 in 1905. In 1909 Argentine imported salt to the value of £104,000 from Spain, and Brazil to the value of £160,000, also from Spain.

temperatures below 30° they both crystallise with $2H_2O$. They are used in medicine and have a similar action to the potassium salts.

SODIUM CHLORATE : $NaClO_3$, which is now obtained electrolytically, and **SODIUM PERCHLORATE**, $NaClO_4$, are more soluble in water than the corresponding potassium salts, and may be economically substituted for them for certain industrial purposes. The methods of preparation are similar to those of the corresponding potassium salts (*which see*). In 1908 Italy produced 220 tons at £32 to £36 per ton at Bussi (Società Elettrochimica of Rome) by electrolysing sodium chloride in the preparation of NaOH and Cl.

In 1914 the output of sodium chlorate in Italy was 232 tons and in 1915 236 tons (£10,384). The imports of sodium and potassium chlorates and perchlorates together into Italy amounted to 364 tons in 1908, 273 in 1910, 179 in 1911, 234 in 1912, 220 in 1913, 144 in 1914, 712 in 1915, and 1499 (£179,800) in 1916; in the last-named year a large new chlorate factory was started at Terni (French company), and this exported 11,943 tons (£1,435,836) to France.

SODIUM IODATE : $NaIO_3$, which also exists with $3H_2O$. This compound is found in Chili saltpetre, from which it is now removed because it appears to be harmful to vegetation when the nitrate is used as a manure. A *periodate*, $NaIO_4$, $3H_2O$, and *superiodate*,  $IO(ONa)_2(OH)_3$, are also known; they have no practical importance, but confirm the variable valency of the halogens.

ALKALI HYPOCHLORITES (BLEACHING SALTS)

Hypochlorites of the alkali metals are formed, together with the chlorides, by passing Cl into a cold solution of sodium hydroxide, but it should be observed that excess of chlorine must not be added, because the unstable hypochlorous acid is then formed, whilst in the hot chlorates are produced :

$$2NaOH + 2Cl = NaCl + H_2O + NaOCl.$$

If sodium carbonate is used instead of the hydroxide, free hypochlorous acid is formed : $Na_2CO_3 + Cl_2 + H_2O = NaCl + NaHCO_3 + HOCl$; chlorate is also produced to some extent, but this may be avoided by allowing the chlorine to act on a solution containing both sodium hydroxide and carbonate, the result being a bleaching solution as active as that obtained electrolytically (Fr. Pat. 420,358 of 1910; *see also* later).

The hypochlorites have a sweetish, disagreeable smell; they are caustic and decompose even under the influence of sunlight, and more easily on heating, forming oxygen, chlorides, and chlorates, as is shown in the following equations :

$$(1)\ 3ClONa = 2NaCl + ClO_3Na. \qquad (2)\ 2ClONa = 2NaCl + O_2.$$

In presence of an excess of alkali hydroxide, the hypochlorites are stable even at a temperature of 50°.

The hypochlorites slowly oxidise and destroy organic dyestuffs; the action is much more rapid and energetic if hypochlorous acid is liberated by means of other very weak acids, such as carbon dioxide. If an excess of a strong acid is employed, the oxidising hypochlorous acid is not liberated, but chlorine is formed instead, as was stated above :

$$NaOCl + 2HCl = H_2O + NaCl + Cl_2.$$

Taylor and Higgins (1911), however, hold that nascent chlorine is liberated even with CO_2.

POTASSIUM and **SODIUM HYPOCHLORITES** : **KOCl** and **NaOCl**, are employed for bleaching vegetable fibres (cotton, linen, etc.), under the name of

Eau de Javelle for the former and *Eau de Labarraque* for the latter.[1] The latter is the more economical and is also prepared by the double decomposition of dissolved calcium hypochlorite and sodium carbonate or sulphate; insoluble calcium carbonate or sulphate is formed and sodium hypochlorite remains in solution. It is now obtained by direct electrolysis in the cold of dilute solutions of sodium chloride without employing diaphragms, the products of the electrolysis ($Cl + NaOH$) being allowed to mix, so that dilute solutions of sodium hypochlorite result directly with evolution of hydrogen: $NaCl + H_2O +$ electric current $= NaOCl + H_2$.

For this purpose various small forms of apparatus are constructed which are adapted for the use of bleaching works. The first plant was the Hermite plant (1883), with cathodes formed of zinc discs alternating with anodes of platinum gauze, and with a bath of magnesium chloride and hydroxide. This had many drawbacks and was gradually replaced by more practical forms of plant, amongst which the best is that which has been devised in recent years by Kellner and is illustrated in Fig. 230. Alternate positive and negative electrodes are placed parallel to one another in an earthenware vessel, *a b*: they consist of a series of ten to twenty glass plates surrounded by iridio-platinum wire. The first and last electrodes where the current enters and escapes are constructed entirely of iridio-platinum gauze. By means of a pump, *g*, the solution of NaCl is forced from the vessel, *h*, through the apertures, *e* and *f*, into the interspace between the individual plates of the electrodes which form so many distinct baths, and on passing the current electrolytic dissociation occurs in each chamber with an E.M.F. of 5 volts; if, therefore, there are 10 chambers in the battery, a total E.M.F. of 50 volts will be required. By means of the pump, *g*, the solution is continually circulated, passing from the upper receiver to the lower through a tube not shown in the figure. In the lower vessel a coil is placed through which cold water circulates in order to prevent the temperature from rising above 20° to 25°. The formation of chlorate, which has no bleaching action, is thus avoided. In an ordinary apparatus, using a solution of 110 kilos of salt in 1 cu. metre of water, a current of 120 amps. is required. The electrodes finally become covered with a little gypsum contained in the salt, and then increase the internal resistance considerably so that the liquid becomes heated. This trouble is overcome by reversing the direction of the current now and again by changing the poles; the deposit then passes into solution.

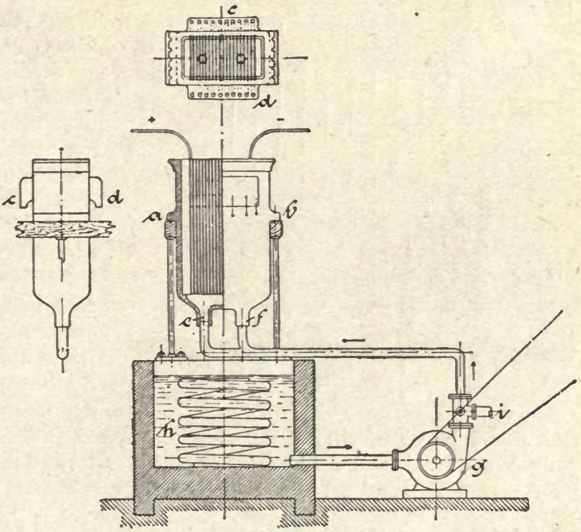


FIG. 230.

A Schuckert apparatus, with one carbon and one platinum pole, is now used, and another type, proposed by Oettel, has two carbon poles and gives good results.

---

[1] After Scheele had discovered chlorine in 1774 Berthelot immediately noted the bleaching properties of this gas and tried to employ it practically in aqueous solution. In 1789 at Javelle, near Paris, another liquid for bleaching purposes was prepared by passing chlorine into a solution of potassium hydroxide. In 1798 Tennant, in Great Britain, obtained a liquid for bleaching purposes by passing chlorine into milk of lime. In 1799 Tennant further found that by the action of chlorine on solid calcium hydroxide a solid product was obtained which was much more stable and easier to transport. The industrial importance of chloride of lime or bleaching powder dates from that time.

A dilute solution (10 per cent.) of sodium chloride is ordinarily employed, because a solution of hypochlorite containing 1·3 grms. of chlorine per 100 c.c. is sufficiently strong, as solutions containing only 0·2 per cent. of active chlorine are effective for bleaching; these solutions are more stable in the dark than when exposed to the light.

A high current density (1000 to 1500 amps. per sq. metre) is generally used. The current yield diminishes rapidly, and in obtaining a 3 per cent. solution of active chlorine there is great waste of current and the hypochlorite is transformed into chloride again at the cathode, while chlorate is formed at the anode. The current yield is improved by the addition of a little $CaCl_2$ and sodium resinate to the liquid and increases also with more concentrated solutions: with a 10 per cent. solution the yield is 50 per cent. and the solution contains 2 per cent. of active chlorine, whereas with a 20 per cent. solution the current yield is still 50 per cent., but the solution contains 3 per cent. of chlorine.

For very small plants the Oettel apparatus with graphite electrodes (made by Haas and Stahl) may be recommended, this giving 1 kilo of chlorine for about 4·8*d.*; the Schuckert type (graphite and platinum), yielding chlorine at 3·35*d.* to 3·85*d.* per kilo, may also be used, but for large plants better results are obtained with the Kellner type with platinum electrodes (3·25*d.* per kilo) or with the Schuckert type with platinum electrodes (2·98*d.* per kilo).

Solutions of sodium hypochlorite produced electrolytically are more active than solutions of bleaching powder, even for equal strengths of active chlorine, because a portion of the hypochlorous acid in the electrolytic solutions is present in the free state, and is much more energetic; when solutions of calcium chloride, $CaCl_2$, are electrolysed, solutions containing much free HOCl are also obtained. Fabrics thus bleached are of a purer, less yellow white than those given by calcium hypochlorite. In order to determine the quantity of this free acid, and, therefore, the quality of the bleaching liquid, it is treated with carefully neutralised hydrogen peroxide and the hydrochloric acid so formed is titrated. HCl is formed by the hypochlorous acid and not by sodium hypochlorite, as is seen by the following equations:

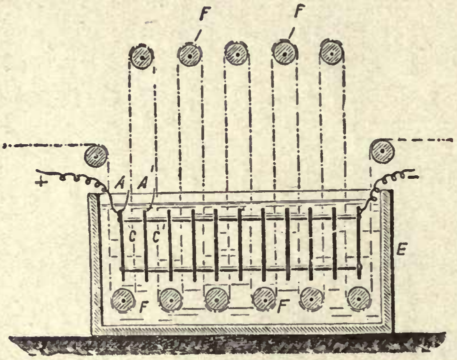


FIG. 231.

$$NaOCl + H_2O_2 = NaCl + H_2O + O_2.$$
$$HOCl + H_2O_2 = HCl + H_2O + O_2.$$

Kellner has also constructed apparatus for bleaching textiles continuously and directly in an electrolytic bath (Fig. 231) by passing the fabric between alternating electrodes, *c* and *c'*, kept apart by glass rods. The fabric passes over rollers, *F*, and is alternately immersed in the bath and withdrawn.[1]

---

[1] Engelhardt (1911) calculates as follows the cost of obtaining an electrolytic bleaching effect equivalent to that given by a ton of calcium hypochlorite, in a plant electrolysing 170 kilos of salt per day (10 hours), the electrolyser using 13·2 kilowatts (120 amps. at 110 volts), which produce 22·2 kilos of active chlorine. A saving of 30 per cent. of the chlorine is assumed compared with the use of calcium hypochlorite, and the price of the salt is taken as 15*s.* per ton; the figures are for 300 working days. Cost of electrodes £270; cost of tanks, pumps, etc., £230. Total for plant, £500. Running expenses: 13·2 × 10 × 300 = 39,600 kw. — hours at 0·24*d.* = £39 12*s.*; 170 kilos of salt per day = 170 × 300 = 51,000 kilos per year at 15*s.* per ton = £38 5*s.*; sinking fund for the platinum (4 per cent.) and maintenance £10 8*s.* + 10 per cent. sinking fund on accessories and maintenance £23 + interest, etc., £11 10*s.* Total £122 15*s.* With a saving of 30 per cent. of chlorine the electrolytic solutions so prepared would correspond with 26·7 tons of calcium hypochlorite, the price of which would thus be £4 12*s.* per ton. If the electric energy is calculated at 0·605*d.* per kw.-hour, use of the electrolytic solution for bleaching would be equivalent to paying £6 16*s.* per ton for calcium hypochlorite (with 35 per cent. of active chlorine). In this comparison the labour is neglected, being about the same in the two cases. Account must of course be taken of the convenience of a continual supply of a fresh electrolytic solution without loss of active chlorine.

The electrical energy used in these plants for direct consumption is rather greater than in the large, special electrolytic plants, since dilute NaCl solutions are treated and the temperature is

In Italy 1047 tons of sodium hypochlorite were produced in 1912, 2437 in 1913, 3159 in 1914, and 3599 (£17,873) in 1915.

In France alkaline hypochlorites are prepared both by electrolysis and by the action of a solution of sodium carbonate or sulphate on concentrated calcium hypochlorite solution. In 1913 the output in France was 6000 tons.

SODIUM NITRATE : $NaNO_3$ (CHILI SALTPETRE)

This is found in great abundance in that part of Chili which is adjacent to Peru (Province of Tarapaca), and in Bolivia, mixed with soil and covered by layers of clay, gypsum, and sodium chloride 1 to 3 metres in depth. The earthy mass from which it is extracted is called *caliche ;* it contains from 15 to 55 per cent. of the nitrate (ordinarily 20 to 25 per cent.) over a distance of 200 to 300 kilometres, and has a thickness of 1 to 5 metres. The *caliche* also contains as impurities sodium perchlorate, sodium iodate (up to ½ per cent.), a little potassium nitrate, and much sodium chloride (up to 20 per cent.). The layer (*crust*) covering the caliche is somewhat hard; the compositions of samples of caliche and crust (in brackets) are: $NaNO_3$, 36·35 per cent. (17 per cent.); NaCl, 32·06 (2); Na_2SO_4, 8·02 (72); $CaSO_4$, 8·02 (2); other salts, KCl, $MgCl_2$, $NaIO_3$, etc., 2·05 (6); insoluble matter, 14·5 (1).

The origin of these important deposits must be sought in the decomposition of enormous accumulations of nitrogenous organic matter in the presence of strong bases (lime, magnesia, soda, etc.), and also in the action of nitrifying bacteria (p. 350). The organic matter must have been of vegetable origin, because in these nitrate deposits phosphates are never found. The nitrate layers remain almost unaltered in these regions because rain is very rare and sometimes does not occur for two or three successive years. The deposits were discovered in 1810, but only since 1830 have they been used as fertiliser.

The *caliche* is ground and lixiviated with hot water, and the solution is concentrated in large iron pans heated by steam coils (from oil-heated boilers) to a temperature of 110°, 1000 parts of $NaNO_3$ passing in solution for 70 of NaCl and 20 of Na_2SO_4. The decanted solution is allowed to cool in numerous vessels exposed to the air, the nitre then crystallising out.

A crude commercial product is thus obtained (for fertilising purposes, etc.), which contains 95 per cent. of $NaNO_3$, 1 to 3 per cent. of NaCl, and 2 per cent. H_2O. Sometimes it contains up to 1 per cent. of sodium perchlorate, which is injurious to vegetation. The mother-liquors are utilised for the preparation of iodine (*see* p. 165). At one time only *caliche* containing more than 20 per cent. of nitrate was treated. To-day, with improved modern plant, a 10 to 15 per cent. raw material is treated.

In modern plants the dissolution of the nitrate contained in the *caliche* is carried out systematically on a counter-current system in batteries of six vessels (2 × 2·5 × 10 metres) heated with steam, the most dilute solution coming into contact with the almost exhausted residue, whilst the solution as it gradually becomes more concentrated traverses the richer *caliche*. The final residues are again washed with water, which is afterwards used in the extraction. The crystallising vessels have a base of 20 × 2 metres and a depth of 2 to 3 metres. The crystals are spread out on floors to dry. The residues deposited on the bottom of the crystallisers contain up to 8 per cent. of the nitrate, but this cannot be recovered even with water. The production of 5000 tons of nitre per month from a 20 to 25 per cent. *caliche* requires 900 cu. metres of dissolving vessels and 6000 cu. metres of crystallisers, the cost of

---

kept low to avoid formation of chlorates; further the current yield diminishes with increase in the dissolved active chlorine, so that part of the NaCl remains unchanged in solution and is lost. Nevertheless, these direct plants are convenient both for bleaching cotton and flax yarn and fabrics, as well as for paper and cellulose manufacture, since the apparatus requires little supervision and the continuous current dynamos used to work them can be used for lighting purposes at night. By their use chlorine is saved, the extent of the saving being 10 to 30 per cent.

such a plant being £100,000. In some plants dissolution of the nitrate is effected in steam-heated apparatus arranged in series and resembling the diffusers employed for dissolving sugar from the beet (*see* Vol. II., "Organic Chemistry").

In order to remove the perchlorate sometimes present in the crude Chili nitrate, the latter is dissolved in the cold in the exact quantity of water corresponding with its solubility; the perchlorate then remains undissolved, being less soluble.[1]

We have already recorded on pp. 347 *et seq.* the processes which are now used for the utilisation of atmosphere nitrogen and for the preparation of nitrogenous substances capable of replacing nitrate for agricultural purposes.[2]

Sodium nitrate crystallises in rhombohedra closely resembling cubes, hence the name of *cubic nitre* in contradistinction to *prismatic nitre*, under which name potassium nitrate is known.

It melts at 318° and is a little more soluble in cold water than potassium nitrate, 80 per cent. being dissolved by water at 0°, 90 per cent. at 20°, 111 per cent. at 50°, 168 per cent. at 100°, and 225 per cent. at 120°. It is somewhat hygroscopic and cannot, therefore, be used in gunpowder. It has the specific gravity 2·20 and the specific heat 0·278.

APPLICATIONS. The great bulk (70 to 80 per cent.) is used as a nitrogenous fertiliser, next in importance being that used for making nitric acid and potassium nitrate (conversion nitrate). It is used in the manufacture of sulphuric acid, in glass works (3 to 4 per cent. by weight on the quartz sand used), and for preserving meat.

In 1910, 150,000 tons were used in Germany for making nitric acid and 50,000 tons in the United States.

STATISTICS AND PRICES. The consumption of Chili saltpetre in different countries is shown in the following table (p. 577).

In view of the enormous consumption, almost doubled from 1900 to 1916, doubts have arisen as to whether the Chilian deposits might not soon be exhausted; various inquiries were made by private companies and by the Chilian Government, which resulted in artificially discordant figures, covering more or less dishonest speculations, and whilst, on the one hand, it was said that the still unexploited deposits could yield a maximum of only 100,000,000 tons of nitre, so that they would be exhausted in thirty to forty years, on the other hand, the results of the inquiry which was made by the engineer Bertrand showed that up to June 1909 the presence of at least 250,000,000 tons of nitrate in deposits containing more than 15 per cent. had been proved. It is also supposed that in the regions which have not yet been definitely explored by the commission of inquiry, double or three times the quantities of nitrate exist, so that there can be no question of exhaustion for 150 or 200 years, even supposing that the annual consumption reaches 4,000,000 tons. We may add that nitrate deposits have been discovered in California in localities provided with water, these containing about 20,000,000 tons of sodium nitrate (the deposits contain from 7·2 to 22·6 per cent. of $NaNO_3$); other very important deposits have been found in the Argentine, but in localities which are not easily accessible.

In any case agriculture will sooner or later have to face the grave problem of a substitute for Chili saltpetre, although good practical results have already been obtained in the direction of the utilisation of atmospheric nitrogen (*see* pp. 347, 366 *et seq.*).

The effects produced by nitrate in agriculture are truly enormous, especially if the fertilisation is completed with superphosphates and potassium salts; in some localities

---

[1] Sodium nitrate to be used for making nitric acid, etc., should contain only minimal proportions of chlorides, iodides, etc., since otherwise the nitric acid would contain hydrochloric acid, etc., injurious for the manufacture of nitroglycerine (*see* Vol. II., "Organic Chemistry"). To eliminate these halogens, Uebel (Ger. Pat. 261,874, 1911) treats the nitrate with a little concentrated sulphuric acid at about 100°, only the halogen hydracids (almost exclusively HCl) being first evolved; these can be condensed apart before introducing the bulk of the nitrate into the nitric acid stills (*see* p. 385).

[2] According to Fr. Pat. 398,738 of 1909, the nitrites which are always formed in the process of electrolytic fixation of nitrogen may be completely transformed into nitrates by heating them to about 300° in presence of NO_2, thus:

$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO,$$

the latter regenerating NO_2 with the oxygen of the air.

IMPORTATION AND CONSUMPTION OF CHILI SALTPETRE IN DIFFERENT COUNTRIES (TONS)

	1890	1900	1905	1909	1910	1911	1912	1913	1914	1915	1916
Germany	344,209	484,544	540,916	665,450	786,000	731,000	812,898	774,000	599,854 (half-yea)	—	—
England	108,000	141,155	104,436	90,200	128,600	130,497	125,560	143,187	174,669	133,631	21,231
France	190,000	285,955	242,629	258,743	345,160	317,725	353,776	322,115	297,180	254,000	540,700
Austria-Hungary . . .	—	54,559	66,740	80,533	81,781	65,781	92,838	93,035	62,733 (half-year)	—	—
Belgium	85,000	153,318	202,241	231,162	257,225	327,707	235,382	304,136	158,482 (half-year)	—	—
Italy	—	27,891	46,517	43,658	61,290	59,635	54,700	67,535	59,850	71,730	85,650
Sweden	—	13,935	22,946	28,804	32,340	31,324	35,107	33,802	41,657	30,908	36,360
Denmark	—	5,773	12,088	20,720	26,049	28,990	35,376	34,930	42,592	—	—
Canada	—	—	—	14,788	19,660	26,143	39,714	36,406	12,047	27,365	38,193
United States . . .	83,000	134,247	282,229	435,300	527,600	553,620	494,156	635,905	550,408	704,581	1,237,975
Spain	—	—	—	33,690	32,695	42,415	46,715	35,235	36,082	38,376	42,015
Japan	2,000 ?	4,000	11,638	6,470	14,080	28,233	19,190	26,726	24,425	30,211	46,021
Holland	—	95,000	126,000	135,600	164,800	190,320	204,169	203,585	149,807	50,857	60,877
Russia	—	—	—	15,663	28,593	31,731	51,644	43,382	53,932	34,120	33,121
Africa (Egypt) . . .	2,500 ?	3,418	21,000	27,000	31,000	49,000	57,000	57,500	53,000	53,500	20,000
Australia	300	3,000	3,083	1,050	6,912	1,432	3,224	3,393	3,400	3,400	5,700
Switzerland	—	—	—	3,768	3,804	4,058	3,162	3,328	2,280	199	343
Exported from Chili . .	1,065,277	1,453,000	1,650,000	2,110,000	2,333,860	2,450,580	2,494,166	2,739,530	1,847,586	2,031,000	2,991,786
Stock at Chilian ports at end of year	—	—	—	1,546,443	1,630,160	1,694,536	1,620,056	1,772,161	1,087,910	789,700	718,315

N.B.—Belgium re-exports part of the nitrate imported.

the production is trebled. It is spread over the ground a little at a time to the amount of 100 to 130 kilos per hectare in all, as it is very soluble and is easily carried away by rain. The plants appear to assimilate the nitrate when it has been transformed into calcium nitrate in the soil (Grandeau).

PRICES. Crude nitrate (95 per cent.) costs £8 16*s.* to £10 16*s.* per ton at the Port of Genoa; when refined by recrystallisation and powdered it cost (in 1910) double, and chemically pure nitrate three times, this amount. When it is refined in Chili by simple clarification of the original hot solution it is whiter and contains 96 per cent. of nitrate; this quality is used industrially and costs only 8*s.* to 16*s.* more per ton than the crude product.[1]

The international trade in the nitre exported from Chili is based on analyses made at Valparaiso in the laboratory of Ed. Wieghmann and Roberts and Fraser on samples taken from the parcel at the port of embarkation. The prices are based on a purity of 95 per cent., and if the percentage is 94 to 95, an allowance of 1 per cent. on the price is made; if 93 to 94, the allowance is 4 per cent.; if 92 to 93, 5 per cent, and if 91 to 92, 6 per cent. For percentages lower than 91, a further allowance of 3 per cent. per unit below 91 per cent. is made. In 1910 the Hamburg Convention decided also that a rebate should be made if the perchlorate exceeds 0·75 per cent.

The price of nitrate has varied somewhat of late years, owing to the formation of a trust by the producers and to the levy of an export tax of £2 11*s.* per ton by the Chilian Government. The trust was, however, dissolved at the end of 1908, the output being then increased and the price lowered. In Italy in 1910 the price per unit of nitrogen in

---

[1] **Analysis of Nitrate.** The moisture is determined by heating 50 grms. to 130° until the weight no longer decreases. The dry product is dissolved in water, filtered, the filter washed and dried, and the quantity insoluble in water deduced from the residue remaining on the filter. The solution is diluted to one litre and the chlorine of the chlorides determined in one portion by titrating it with a normal solution of silver nitrate. The sulphates are precipitated with barium chloride and the separated barium sulphate washed, ignited, and weighed. The perchlorates are determined in 10 grms. of nitrate in which the chlorides have already been determined. The sample is melted in a covered porcelain crucible with sodium carbonate free from chlorine; after 10 to 15 minutes no further bubbles of gas are evolved, and the mass is dissolved in nitric acid, diluted, and the additional quantity of chlorine formed from the chlorates then determined with standard silver nitrate solution; the remaining matter is considered to be nitrate. Commonly, however, the nitrate is itself determined with Lunge's nitrometer, of which we give an illustration in Fig. 232. 0·35 grm. of the nitrate is weighed and placed in the little open cup at the top of the Figure, to the left; the tube *A* has been previously filled with mercury by suitably raising the tube *C*, which is also filled with mercury, and allowing the air to escape from *A* by means of the cock, *O*. As much air is allowed to enter *B* as corresponds with 100 c.c. of air at 0° and 760 mm. under the conditions obtaining at the time; this will necessarily be more than 100 c.c., and is found from tables. By this means the necessity of reducing the volumes of the gas to 0° and 760 mm. afterwards is avoided. The nitrate is dissolved in a very small quantity of water, and then by lowering the tube *C* and opening the cock, *O*, the solution, but no air, is allowed to enter *A*; 3 to 4 c.c. of strong sulphuric acid are poured in small portions into the small cup and allowed to enter *A* each time. The nitrate solution, acid, and mercury are then shaken vigorously together, this causing the nitrogen in the nitrate to be evolved in the form of NO gas. In order to read the volume of gas so formed, the tube *C* is raised until the mercury in *B* reaches the 100 c.c. mark. *B* and *C* are then lowered simultaneously, until the mercury in *B* at the 100 c.c. mark is at the same level as the mercury in *A*, which contains the NO, and the volume which this occupies is read off, as it is now corrected to 0° and 760 mm. Each cubic centimetre of NO corresponds with 0·003789 grm. of $NaNO_3$. In the Figure a small bottle is also seen connected with the nitrometer at the left-hand top corner; this is used when it is necessary to evolve gas outside the instrument, for example, in the analysis of H_2O_2, which evolves a definite volume of oxygen in contact with MnO_2. Use may also be made of a nitrometer with two tubes, *A* and *C*, the graduated one having a bulb of about 50 c.c. below the tap; to measure the gas at the atmospheric pressure, the non-graduated tube is raised slowly and the tap is cautiously opened from time to time until the gas just tends to overcome the pressure of the drop of acid in the orifice of the cock. The gas is then under atmospheric pressure and the volume is reduced to 0° and 760 mm. by means of tables.

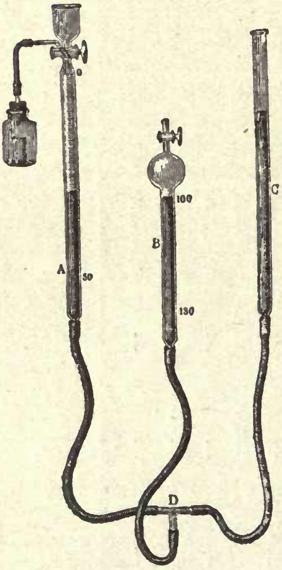


FIG. 232.

sodium nitrate (at 95 per cent. it contains 15·6 units) was 12·5*d.*, whilst the unit in ammonium sulphate cost 14·8*d.*; these prices and also their relationship vary every year. At the port of Dunkirk nitrate cost £7 per ton in 1898, £8 4*s.* in 1901, £8 16*s.* in 1903, £10 in 1905, £10 16*s.* in 1908, £9 4*s.* in 1909, £8 8*s.* in 1910, £9 12*s.* in 1911, and £10 in 1913. The transport of nitrate from Chilian ports to European ports by sailing-ship costs about 12*s.* per ton, which is less than the freight from Genoa to Brescia; by steamer it costs 17*s.* 6*d.* to 19*s.* 2*d.*, besides 1·5*d.* to 2*d.* for loading.

During the European War Germany replaced all the Chilian saltpetre it used by synthetic nitric acid, nitrates and ammonium salts (*see* pp. 347, 366, and 390). In Italy, owing to the difficulty of sea transport, nitrate rose to £56 per ton (July, 1917).

In 1911 there were 77 companies engaged in extracting nitrate in 142 works (of which 24 were shut), the exports being valued at £24,000,000 and the tax paid to the Chilian Government £6,400,000. As a bye-product, 500 tons of iodine, worth £400,000, are obtained.

SODIUM NITRITE : $NaNO_2$. This compound is obtained by melting sodium nitrate in iron pans furnished with stirrers and adding portions of lead a little at a time, keeping the temperature between 400° and 420°, as otherwise the iron pan is destroyed. The molten lead should all be transformed into oxide. The fused mass is poured into water and neutralised with dilute sulphuric acid or nitric acid (as a little NaOH, etc., is formed), the lead remaining in the form of oxide. The aqueous solution of the nitrite is concentrated in open pans to 42°–45° Bé. (in the hot), and is then poured into vessels in which it crystallises; it is then centrifuged and dried at 50°. In this way it is possible to transform as much as 93 per cent. of the nitrate into nitrite, which is obtained fairly pure (up to 98 per cent.) by a further crystallisation.

A better yield is now obtained by mixing a concentrated solution of sodium nitrate with quicklime; the solution is heated until it is saturated and a current of SO_2 free from air is then passed through :

$$NaNO_3 + CaO + SO_2 = SO_4Ca + NaNO_2.$$

Dittrich, on the other hand (Ger. Pat. 212,203 of 1908), reduces the nitrate by mixing it to a paste with sawdust (charcoal and graphite produce a violent and irregular reaction); it is then melted in open pans, extracted with water, and the solution concentrated to 45° Bé. and allowed to crystallise.

A molten mixture of sodium nitrate and sodium hydroxide has also been used and heated to 320–400°, anhydrous sulphite being then added (*see* Potassium Nitrite).

According to Pellet and Corni (1907) better yields are obtained by reducing the nitrate with coke and iron turnings. J. Grossmann (Ger. Pat. 160,671) obtains the nitrite by fusing sodium nitrate in an iron vessel and adding gradually a mixture of lime and graphite; the nitrite is extracted from the resulting yellow mass by means of water.

During the manufacture of synthetic nitric acid by the electric process (p. 391) nitrite is obtained, and at Notodden in Norway 2700 tons were produced in 1909. Indeed, most of the nitrite now consumed in Europe comes from Norway.

Sodium nitrite crystallises (hexagonal prisms) more easily than potassium nitrite and is less deliquescent; it dissolves easily in 90 per cent. alcohol. Sodium nitrite solution has an alkaline reaction.

Nitrites may be distinguished from nitrates by adding them to a hot concentrated solution of sodium hydrosulphite; nitrites evolve ammonia whilst nitrates remain unaltered.

USES. Sodium nitrite is largely used in making azo dyestuffs and in dyeing by diazotisation of various colours on the fibre itself (cotton, silk, etc.; *see* Vol. II., "Organic Chemistry"). The production of azo colours in France requires about 500 tons of the nitrite per annum.

Commercial sodium nitrite used to cost about £34 per ton, but during the

European War the price in Italy rose to £180. The chemically pure product, in sticks, cost 3*s*. per kilo prior to the war.[1]

Germany is the largest consumer of sodium nitrite, on account of the great importance of its aniline dyestuff factories, and has to supplement its own production by considerable imports, which were 1617 tons in 1908 and 2634 tons in 1909, the exports being 754 tons; in 1913 France produced 1000 tons and exported 400 tons.

SODIUM SULPHATE : Na_2SO_4

This compound is found ready formed in large saline deposits in Spain (Toledo), at Tiflis, in Siberia, in Sicily, both with and without water of crystallisation, and in many mineral waters. It is found crystallised without water in the form of *thenardite*, Na_2SO_4, and with water as *mirabilite* or *Glauber's salt*, $Na_2SO_4, 10H_2O$. It is found at Stassfurt in monoclinic crystals as *glauberite*, $Na_2SO_4, CaSO_4$. There are important Glauber's salt deposits in Italy in the Province of Caltanisetta. An American company has proposed the utilisation of natural sodium sulphate from the Caspian Sea for the manufacture of sodium carbonate and hydroxide on the spot, as is already done with the Glauber's salt deposits in Eastern Siberia.

It is obtained also from the mother-liquors of sea-salt, which contain magnesium sulphate and NaCl; this solution separates sodium sulphate by double decomposition on evaporation and cooling.

At Stassfurt it is produced industrially by utilising the mother-liquors from the treatment of carnallite or kieserite, which still contain about 25 per cent. of magnesium sulphate and 50 per cent. of sodium chloride. These solutions are evaporated to a concentration of 34° Bé., at a temperature of 33°; they are then allowed to crystallise during the cold winter nights in large tanks (28 metres × 22 metres × 21 cm. deep):

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

The crystals which separate contain 10 mols. of water. On starting directly from solutions of magnesium sulphate, instead of using the theoretical proportions, $MgSO_4$ and 2NaCl (that is, about 100 to 100), the double quantity of NaCl is used, *i. e.*, 100 kilos of $MgSO_4$ and about 200 kilos of NaCl; in this way a more complete separation of sodium sulphate is obtained although only about half of the magnesium sulphate is transformed into the sodium salt.

Most commercial sodium sulphate is produced in the Leblanc soda works or hydrochloric acid works by heating sodium chloride with sulphuric acid in furnaces (*see* p. 173). It is also obtained in large quantities by the Hargreaves-Robinson process (*see* p. 177).

When pure sodium sulphate is required, the crude salt is dissolved in boiling water to saturation; the acid which is present is then neutralised with milk of lime, and a solution of chloride of lime is added with vigorous stirring until all the iron is precipitated. The hot solution is poured into lead-lined wooden vats. Crystals of $Na_2SO_4, 10H_2O$, containing

---

[1] Nitrites may be determined quantitatively, even in presence of nitrates and organic matter, by heating the mixture with a solution of ammonium chloride of known strength; the whole is then concentrated to a few cubic centimetres, taken up with water and distilled in the presence of magnesia, the ammonia formed from the residual ammonium chloride which is not decomposed by the nitrite being collected in standard sulphuric acid. The loss of ammonia, compared with that originally present in the ammonium chloride which was added, allows the quantity of nitrite to be calculated; nitrates do not react.

Sodium nitrite may also be determined when mixed with nitrates by the method of W. M. Fischer and Steinbach (1910), by adding methyl alcohol and then dropping in a known volume of titrated sulphuric acid, and passing through the mixture a current of air, this carrying over the methyl nitrite, which is instantaneously and quantitatively formed (boils at − 11°).

Maderna and Coffetti (1908) measure the quantity of nitrogen dioxide which is formed on treating the mixture with potassium ferrocyanide in presence of acetic acid in Lunge's nitrometer; this gas is formed from the alkali nitrite, while the nitrates remain unchanged. In order to avoid errors in reading the volume of gas, due to the vapour pressure of acetic acid, these authors have replaced the latter by a concentrated solution of citric acid.

The strength of nitrites in general is determined with a standard solution of potassium permanganate, according to Lunge, the estimation being based on the reaction recorded on p. 381.

56 per cent. of water of crystallisation, are thus obtained in large or in small pure crystals, according to whether the solution has been cooled slowly and quietly or rapidly with stirring. The dissolution of 1 mol. of Glauber's salt in 400 mols. of water is accompanied by the absorption of − 18·76 cals.; by mixing 5 parts of Glauber's salt with 4 parts of sulphuric acid the temperature is lowered from + 10° to − 16°, whilst 8 parts of Glauber's salt and 5 of hydrochloric acid give a lowering from + 10° to − 17°. Saturated solution of Glauber's salt freezes at − 1·25° (pure ice separating) and boils at + 104°.

Sodium sulphate crystallises from cold aqueous solutions at temperatures below 30° in large monoclinic, colourless, and transparent crystals, $Na_2SO_4 + 10H_2O$ (containing 56 per cent. of water), which become covered with a white powder of anhydrous sodium sulphate by efflorescence in the air. At 34° this Glauber's salt melts in its own water of crystallisation and a portion of the anhydrous sulphate separates. This melts at about 886°, and then has the sp. gr. 2·104 and is not reduced by CO. A mixture of NaCl and Na_2SO_4 melts at 600° (NaCl alone at 815°).

The anhydrous sulphate is easily obtained by Pechiney's method, by heating the crystallised salt to 40° to 50°, when it melts in its water of crystallisation to a supersaturated solution, and then adding $MgSO_4$, or NaCl, or a mixture of these two salts. On stirring, the anhydrous sulphate separates, because the concentration of the SO_4'' anions or $Na^{\cdot}$ cations has been increased (*see* pp. 103, 542). By the action of 16 parts of NaCl on 100 parts of Glauber's salt 90 per cent. of the latter is separated as the anhydrous sulphate; in certain cases this operation is carried out in order to economise cost of transport. A partial dehydration may also be obtained by letting the finely crystallised or powdered Glauber's salt stand in the air for some time, stirring it up repeatedly. The phenomenon of efflorescence then allows the anhydrous salt to be obtained because the pressure of the water vapour of the crystallised salt is higher than the mean vapour pressure of the moisture in the air, and thus the water of crystallisation evaporates; anhydrous sulphate obtained in this way is lighter and very voluminous. This very economical process can be carried out with advantage in hot climates such as that of Sicily, so that the sulphate may become lighter and may be carried a long distance at small expense.

The varying solubility of this salt with alteration of the temperature, which acquires a maximum of 34°, is of interest:

100 parts of water at	0°	dissolve	12	parts of $Na_2SO_4 + 10H_2O$
,, ,,	18°	,,	48	,, ,, ,,
,, ,,	25°	,,	100	,, ,, ,,
,, ,,	30°	,,	200	,, ,, ,,
,, ,,	34°	,,	354	,, ,, ,,
,, ,,	50°	,,	263	,, ,, ,,
,, ,,	100°	,,	238	,, ,, ,,

Since the solubility diminishes above 34° we must suppose that above this temperature the molecules of $Na_2SO_4, 10H_2O$ are decomposed with separation of the anhydrous sulphate, and that the solubilities above 34° refer therefore to anhydrous sodium sulphate, Na_2SO_4. This phenomenon has not yet, however, been satisfactorily explained theoretically.

The fact is also interesting that a saturated solution of sodium sulphate at 34° may be cooled down to the ordinary temperature without the smallest trace of separation of the crystals, even on shaking the solution strongly, in spite of the fact that its solubility at that temperature is much less. The solution is, therefore, extraordinarily supersaturated or in a metastable condition.

If, however, to this supersaturated solution, which must be kept in flasks closed with a stopper or with a plug of cotton wool, a trace of atmospheric dust or any body which has been in contact with the air, such as a glass rod, is introduced, the solution immediately becomes solid, forming a compact crystalline mass (labile phase of the supersaturated solution), while a certain quantity of heat is developed, because in general substances in the liquid state or in solution have a higher latent heat than when in the solid state. Crystals of $Na_2SO_4 + 6H_2O$ sometimes separate from the supersaturated solution at 10°; they easily decompose in the air, forming anhydrous Na_2SO_4. According to Arndt, when a sodium sulphate solution is heated to boiling in a platinum dish, it tends to become alkaline and becomes neutral again in the cold.

APPLICATIONS. The greater portion of the sodium sulphate which is produced is employed in the manufacture of sodium carbonate by the Leblanc process. It is used, especially in the anhydrous state, in the manufacture of glass, ultramarine, and sodium sulphide, and as Glauber's salt in the dyeing of cotton and wool, in making coal-tar dyestuffs and their intermediate products and for making sulphate cellulose, as well as for obtaining freezing mixtures and for transforming organic calcium salts and organic acids into sodium salts. In medicine and veterinary practice it is used as a purgative. A good commercial sulphate may have an acidity of 1 per cent. (expressed as H_2SO_4) and may contain up to 0·5 per cent. NaCl and 0·1 per cent. Fe, but for white glass it should not contain more than 0·02 per cent. Fe, and is then made from raw materials free from lead and in lead-lined vessels.

STATISTICS AND PRICES. The commercial price of crystallised sodium sulphate (containing 56 per cent. of water of crystallisation) is £1 12*s.* to £2 per ton.

In 1905 Germany produced 68,455 tons and exported 48,470 tons of the anhydrous sulphate at £1 10*s.* per ton; in 1908 78,500 tons were exported and 44,404 tons imported, and in 1910 89,200 tons were exported.

The Glauber's salt produced by Germany amounted to 71,410 tons in 1895, 90,368 in 1900, 68,454 in 1905, 80,347 in 1907, and 72,667 tons (£1,000,000) in 1908.

In 1908 Austria imported 7,596 tons and exported 2,558 tons of Glauber's salt.

England exported 35,000 tons of sodium sulphate in 1909 and 58,500 (£108,635) in 1911.

France exports on the average 25,000 tons of the anhydrous sulphate annually; in 1909 Russia produced 70,000 tons; in 1893 Italy produced 4900 tons of the anhydrous sulphate and 1000 tons of crystals; in 1902 it produced 5300 tons of the anhydrous sulphate and 868 tons of crystals (Glauber's salt); the former was used for glass-making, the latter for dyeing; in 1908 the production was 11,500 tons of anhydrous sulphate, valued at £22,732, and 6542 tons of Glauber's salt, valued at £11,858; in 1912 19,000 tons of anhydrous sulphate, in 1914 6987 of Glauber's salt and 15,300 anhydrous, and in 1915, 8750 of Glauber's salt and 14,147 of anhydrous; in 1904 Italy imported 9790 tons of anhydrous sulphate (at £1 12*s.*), which was mainly supplied by Marseilles for use in the glass-works of the Western Italian coast. In 1908 the imports rose to 17,836 tons, of which four-fifths were supplied by France and one-fifth by England; in 1909 the imports were 12,353 tons, in 1910 14,844, in 1911 14,352, in 1912 14,125, in 1913 103,71 (£22,818), in 1914 8982, in 1915 10,607, and in 1916 22,125 tons (£61,950).

The marked increase in the importation in 1916 was due to the large consumption in the explosives factory at Cengio for the manufacture of synthetic phenol required for the preparation of picric acid (*see* Vol. II., "Organic Chemistry"); at the present time, however, the sulphate is produced on the spot.

SODIUM BISULPHATE : $NaHSO_4$ (Acid Sodium Sulphate, Primary Sodium Sulphate, Sodium Hydrogen Sulphate). This compound is formed by the action of sulphuric acid on NaCl or on the normal sulphate at moderate temperatures.

It is formed industrially during the first phase of the decomposition of NaCl by H_2SO_4 in the manufacture of HCl, but it is obtained more especially in the manufacture of nitric acid (p. 383) from sodium nitrate and sulphuric acid, but always retains a little sulphuric acid:

$$NO_3Na + H_2SO_4 = NO_3H + SO_4HNa.$$

From its aqueous solutions, or, better, on concentration of a solution of sodium sulphate in dilute sulphuric acid at 50°, it crystallises at the ordinary temperature with $1H_2O$, whereas, when a solution of 1 part of Na_2SO_4 in about 7 parts of sulphuric acid is cooled, *sodium quadrisulphate*, $NaH_3(SO_4)_2$, is formed, the anion HSO_4' dissociating in its turn into SO_4'' and $H^{\cdot}$. When the aqueous solution is concentrated a hydrate with $3H_2O$ is formed, this melting in the hot and losing all its water of hydration suddenly at 150° (*see* Nitric Acid, p. 386). At a red heat the acid sulphate yields sodium sulphate and pyrosulphate (*see later*), while, when heated with silica at a high temperature, it gives a mixture, $SO_2 + O + H_2O$, suitable for forming sulphuric acid catalytically (*see* p. 319 and Ger. Pat. 265,835, 1912). According to Ger. Pat. 274,873 of 1913 by the Metallbank of Frankfort, the bisulphate may in a suitable furnace be converted continuously into sodium sulphate and sulphuric acid.

It is used as an acid flux at high temperatures and often replaces sulphuric acid in dyeing, so that the acid action of the dye-bath may take effect gradually, this being advantageous in certain cases in order to obtain uniform shades on wool. A bisulphate solution with 5–7 per cent. of acidity serves to replace hydrochloric acid in the cleaning of sheet-iron to be zinced or tinned.

Nitric acid works are often embarrassed by the large quantities of sodium bisulphate which cannot be utilised, in spite of the fact that every 100 kilos corresponds with 60 kilos of sodium sulphate and 35 kilos of sulphuric acid; in Germany this bisulphate is valued at 10*s.* per ton. Certain works situated near the coast get rid of it by dropping it into the sea.

Other uses for bisulphate are mentioned on p. 387.

Italy produced 1600 tons of sodium bisulphate, worth £2,560, in 1908, but later the output increased enormously in proportion to the amount of nitric acid produced (*see* p. 387), and during the war Italian explosives factories alone had an output of more than 40,000 tons of the bisulphate, scarcely any of which was utilised.

SODIUM PYROSULPHATE, $Na_2S_2O_7$,[1] is formed by the action of SO_3 on powdered NaCl, pyrosulphuryl chloride (*see* p. 330) being also produced. It may be obtained, together with the normal sulphate, by heating the bisulphate to 400–500° (*see* p. 315, or by dissolving Na_2SO_4 in hot fuming sulphuric acid, the solution depositing a mixture of sodium bisulphate and pyrosulphate on cooling. At a red heat (600°) the pyrosulphate decomposes into normal sulphate and SO_3 ($Na_2S_2O_7 = Na_2SO_4 + SO_3$ and a little SO_2).

SODIUM SULPHITE: Na_2SO_3. This compound is prepared as follows: A measured quantity of aqueous sodium hydroxide solution is saturated with SO_2 and acid sodium sulphite thus formed. A quantity of sodium hydroxide solution equal to that already taken is then added, which transforms the bisulphite into normal sulphite, Na_2SO_3, which crystallises out on cooling as $Na_2SO_3 + 7H_2O$. Instead of the sodium hydroxide solution sodium carbonate solution may be employed. In this case bicarbonate is first formed, which then evolves CO_2.

In the air the crystals lose part of their water, becoming opaque by efflorescence and undergoing partial oxidation. It is very soluble in water, the heat of solution being $-5{\cdot}55$ Cals. The solubility is a maximum at 33°. At 150° the water of crystallisation is lost without fusion occurring. At a high temperature it melts, forming a reddish mass of Na_2S (1 mol.) and Na_2SO_4 (3 mols.). It is thought that a hydrate, $Na_2SO_3 + 10H_2O$, exists, large prisms separating when a concentrated solution is evaporated over sulphuric acid. From strongly alkaline solutions of bisulphite, the latter crystallises out without water of crystallisation.

Sodium sulphite is a *reducing agent*, as it easily abstracts oxygen from other substances, forming sodium sulphate. The presence of traces of certain substances (negative catalysts, p. 71) sometimes suffices, however, to prevent the oxidation of the sulphite; traces of mannitol act in this way. Sodium and potassium sulphites are neutral and odourless, but in aqueous solution they have an alkaline reaction. Sulphites of other metals are insoluble in water, but they may be dissolved in aqueous SO_2.

---

[1] The sodium salt of pyrosulphuric acid, $HO.SO_2.O.SO_2.OH$, is obtained by the union of SO_3 or of chlorosulphonic acid ($Cl.SO_2.OH$) with sulphuric acid (monohydrate), so that it is certainly present in oleum, from which it separates in the cold in transparent, crystalline masses, melting at 35°. In the hot it gives $SO_3 + H_2SO_4$. When oleum is cooled to $-10°$, a crystalline compound, $H_2S_2O_7 + 2H_2SO_4$, melting between 10° and 26°, separates out.

For its production on a large scale the process of Basse and Faure is used. Large crystals of sodium carbonate, $Na_2CO_3 + 10H_2O$, are placed in a lead-lined wooden vat with a perforated false bottom (Fig. 233). The current of SO_2 is introduced below through the tube *d* and transforms the sodium carbonate into sodium bisulphite. The unabsorbed SO_2 passes through the soda crystals, and if any still remains free it escapes along with the CO_2 from the tube *c* and bubbles through another soda solution in which all the SO_2 is absorbed. The bisulphite solution obtained has the density 35° Bé. It is neutralised with the necessary quantity of crystallised soda and then concentrated in shallow iron or leaden dishes to 40° Bé. and allowed to crystallise in cast-iron vessels. A solution of 40–45° Bé. may be obtained direct in the apparatus without evaporation, but in practice this is not convenient, since if the density exceeds 36° Bé., the liquid crystallises too readily and blocks the discharge tubes.

APPLICATIONS. Sodium sulphite is used industrially as an *antichlor* (instead of thiosulphates, which were once used) in order to eliminate chlorine from paper or cotton which had been bleached with chlorine, because chlorine yields HCl and oxygen with water and this transforms the sulphite into sulphate. It is employed when SO_2 is required in small quantity, all its sulphur being evolved in this form when it is treated with a dilute acid. It is used as a weak bleaching agent for delicate fibres, such as silk and wool. It is also added, in order to prevent the sugar from turning brown, to sugar juices which are to be concentrated in open pans. It serves also to preserve organic and food substances (to retain the red colour of sausages or preserved meat, 0·1–0·2 per cent. is added). Solutions of sulphite and thiosulphate dissolve silver salts and are therefore used in photography. Sulphites may be detected in presence of sulphates and thiosulphates by precipitating the three products with lead nitrate from 5 c.c. of a 1 per cent. solution; 5 to 6 c.c. of a 12 per cent. solution of sodium thiosulphate are then added with stirring, and the whole is filtered. Lead sulphite, $PbSO_3$, alone remains on the filter and is well washed and the residue treated on the filter with dilute sulphuric acid, which forms SO_2, recognisable by its smell, while the acid filtrate decolorises potassium permanganate solution. Crystallised commercial sodium sulphite, in trucks, costs £8 per ton, and the purer commercial powder £10 per ton. The anhydrous sulphite is sold at £28 per ton, whilst potassium sulphite costs £70 per ton.

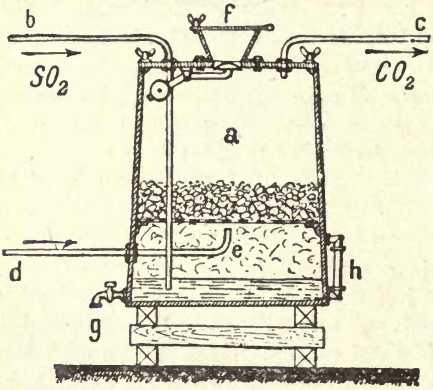


Fig. 233.

Italy produced 1028 tons of sodium sulphite in 1907, 470 (£4206) in 1908, 140 in 1914, and 89 in 1915; also 158 tons (£3168) of sulphites, bisulphites and thiosulphates were imported in 1908 and 1658 tons in 1910. In 1908 Germany exported 2387 tons of sulphite and in 1909 3047 tons.

SODIUM BISULPHITE : $NaHSO_3$. This compound is obtained by the method described above and is used as a very energetic antichlor for vegetable textile fibres, in paper manufacture, etc., when a chlorine bleach has been applied. It is less soluble in water than the sulphite, but oxidises much more easily. The solution has an acid reaction; the heat of solution is – 2·62 Cals. at 10°.

The aqueous solution and also the crystals lose SO_2. Besides SO_2, vapours of sulphur are evolved when bisulphite crystals are heated: $4NaHSO_3 = 2Na_2SO_4 + SO_2 + S + 2H_2O$. Bisulphite with water of crystallisation does not appear to exist. With dilute acid it emits all its sulphur as SO_2 (60 per cent.), even in the cold. Evaporation of a hot concentrated bisulphite solution results in separation of a crystalline mass of *sodium metabisulphite* or *pyrosulphite*, $Na_2S_2O_5$. Sodium bisulphite stable in the air may be obtained by saturating a saturated sulphite solution in the hot with SO_2 and centrifuging and drying in a vacuum oven the crystals which separate.

It is used in dyestuff factories as an energetic bleaching agent for wool and silk, and serves also for preparing soluble tanning extracts, making thiosulphate, preserving wine, beer, etc. Bisulphites are all soluble in water, the solutions having a strong smell of SO_2.

In concentrated solution at 36–38° Bé. sodium bisulphite costs about £4 16*s.* per ton,[1] or at 32° Bé. £2 16*s.* per ton. The crude crystalline product, in grey powder, costs £10 per ton, and the pure anhydrous three times this amount. As it always contains impurities, it should be bought on the basis of the content of SO_2, determined iodometrically.

Italy produced 182 tons of sodium bisulphite in 1904, 310 tons (£1064) in 1905, 809 (£2356) in 1908, 590 in 1909, 1324 in 1910, 887 in 1913, 1262 (£3490) in 1914, and 1031 in 1915. A large proportion of the bisulphite is, however, produced by manufacturers who consume it. France in 1900 produced 2600 tons, 1400 tons being used to make calcium bisulphite and 400 tons for sodium sulphite. In 1913 France imported 585 tons of bisulphite and 163 of metabisulphite.

SODIUM THIOSULPHATE : $Na_2S_2O_3 + 5H_2O$. This compound is also incorrectly called sodium hyposulphite. It is obtained in large quantities from the sulphurised residues obtained in the manufacture of Leblanc soda. These residues are allowed to oxidise in the air and then form calcium thiosulphate which is soluble in water. On boiling the solution with sodium sulphate insoluble calcium sulphate is deposited, and there remains a solution of sodium thiosulphate, which can be concentrated.

It is also formed by boiling an aqueous solution of sodium sulphite with sulphur for a couple of hours : $SO_3Na_2 + S = S_2O_3Na_2$, and also by passing a current of air at 150° into a solution of sodium hydrosulphide :

$$2NaHS + 2O_2 = H_2O + Na_2S_2O_3.$$

According to Ger. Pat. 267,872 (1912), anhydrous thiosulphate is obtained by concentrating the aqueous solution in a vacuum in presence of half its volume of aniline.

It is very highly soluble in water (1 : 1 at 15°), forming slightly alkaline solutions. The heat of solution is — 5·8 Cals.; 100 parts of water at 0° dissolve 50 parts of the anhydrous salt, 69·5 parts at 20°, 104 parts at 40°, and 192 parts at 60°. It is insoluble in alcohol. It crystallises with $5H_2O$ in large transparent prisms stable in the air. At 56° it melts in its water of crystallisation, which it loses at 200°, while at higher temperatures (400°) it decomposes into a yellowish-brown mass of Na_2SO_4 and Na_2S_5.

The alkaline earth thiosulphates are but little soluble, and those of the heavy metals insoluble in water, although they readily combine with the alkali thiosulphates to form double salts soluble in water.

---

[1] Solutions of Sodium Bisulphite at 15° :

Specific gravity	Degrees Baumé	Per cent. of $NaHSO_3$	Per cent. of SO_2	Specific gravity	Degrees Baumé	Per cent. of $NaHSO_3$	Per cent. of SO_2
1·008	1	1·6	0·4	1·171	21	16·5	10·2
1·022	3	2·1	1·3	1·190	23	18·5	11·5
1·038	5	3·6	2·2	1·210	25	20·9	12·9
1·052	7	5·1	3·1	1·230	27	23·5	14·5
1·068	9	6·5	3·9	1·252	29	25·9	15·9
1·084	11	8·0	4·8	1·275	31	28·9	17·8
1·100	13	9·5	5·7	1·298	33	31·7	19·6
1·116	15	11·2	6·8	1·321	35	34·7	22·5
1·134	17	12·8	7·8	1·345	37	38	23·6
1·152	19	14·6	9·0				

The aqueous solution, when exposed to the air and light, forms sulphite, sulphate, free SO_2 and sulphur; it is decomposed by acids with evolution of SO_2 and separation of sulphur. It easily forms supersaturated solutions, which crystallise instantaneously with evolution of heat immediately a crystal of the thiosulphate is added. It acts as a strong reducing agent. It transforms Cl, Br, and I into the respective halides, NaCl, NaBr, and NaI, and is therefore used as an antichlor in the bleaching of cotton and paper, as it eliminates the last traces of chlorine remaining in the fibre after bleaching (*see above*: sodium sulphite); it dissolves lead sulphate and with iodine it forms sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 = 2INa + S_4O_6Na_2,$$

and this reaction is used in analytical chemistry for the quantitative determination of iodine. It is used in photography as a fixing agent, because it dissolves the silver salts at those points of the plate which have not been influenced by light, forming soluble double salts (*see above*). For such purposes it should be purified by recrystallisation from water.[1] It is used also in dyeing, as a mordant in textile printing, in tanning, in the extraction of silver, in gold and silver electroplating, in making aniline dyes, and in medicine as an antiseptic and purgative.

The commercial crystalline product costs £6 8*s*. to £7 4*s*. per ton; the less impure product £8 (in 1918, during the European War, it rose to £44), and the chemically pure £20. In Italy 10 tons were produced in 1905, 215 (£1742) in 1908, 250 in 1909, 340 in 1913, 500 in 1914, and 412 (£3869) in 1915. In 1918 the factory at Cengio alone produced about 5 tons per day. In 1913 France imported 107 tons and in 1915 807 tons.

SODIUM HYDROSULPHITE (Hyposulphite): $Na_2S_2O_4$. This is an energetic reducing agent which is easily oxidised by the air and precipitates various metals from their solutions (Ag, Cu, Hg, etc.). It is used in dyeing, for bleaching textile fibres (and leather, feathers, furs, horsehair), and as a special reducing agent in indigo vats, as it reduces indigo blue to indigo white; in the printing of fabrics it is used as a discharge for the colours. It is also used for bleaching soaps, oils, sugar syrups, etc. (*see* Vol. II., section on Cane Sugar); it is a good reducer for organic nitro- and azo- derivatives and fixes atmospheric oxygen quantitatively. Freshly prepared solutions have the greatest reducing power; after an hour three-fourths of the hydrosulphite (which has a neutral reaction) is transformed into sodium bisulphite with an acid reaction:

$$S_2O_4Na_2 + O + H_2O = 2NaHSO_3.$$

The hydrosulphites are used to distinguish nitrates from nitrites (p. 579). With ammoniacal copper solution they give first a yellow and then an orange coloration, metallic copper finally separating. With dilute copper solution, free hydrosulphurous acid or its salts give a fine red coloration (copper hydrosol), which deposits the copper quantitatively in the hot, whilst other metals present (Fe, Zn, Ni, Co, in acid solution) are not precipitated. Silver and gold are, however, precipitated (together with a little sulphur): $Na_2S_2O_4 + CuSO_4 = Cu + Na_2SO_4 + 2SO_2$; cadmium in acid solution is precipitated as sulphide, mercury as metal.

The hydrosulphites are prepared by dissolving zinc in solutions of sodium bisulphite (with which hydrogen is not developed) and precipitating the dissolved zinc with milk of lime or sodium carbonate solution.

---

[1] The pure salt should contain neither sulphides, nor sulphites, nor pyrosulphites, nor sulphates, so that the solution should give no black precipitate with lead acetate and excess of potash (sulphides), and when boiled with acetic acid until all smell of SO_2 disappears and then filtered, it should give no precipitate with barium chloride (sulphates, or possibly sulphites).

Schutzenberg attributes to hydrosulphurous acid the formula H_2SO_2, whilst according to Bernthsen this would be sulphoxylic acid, which is not known free but exists in combination, whereas hydrosulphurous acid would be $H_2S_2O_4$, sodium hydrosulphite being formed according to the following equation:

$$4SO_3HNa + Zn = Na_2S_2O_4 + Na_2SO_3 + ZnSO_3 + 2H_2O.$$

To increase the yield, Bernthsen and Bazlen (1900) carry out the reaction in presence of SO_2:

$$2SO_3HNa + SO_2 + Zn = ZnSO_3 + Na_2S_2O_4 + H_2O;$$

they prepare a solution of 11° Bé. for direct use by treating 25 kilos of sodium bisulphite (in solution at 40° Bé.) with 54 kilos of an aqueous solution of SO_2 at 4° Bé. (or the corresponding quantity of gaseous SO_2), and then adding, slowly and with shaking and cooling to keep the temperature at 30–40°, 4·2 kilos of zinc dust; after a rest of a couple of hours, milk of lime made with 4·2 kilos of CaO and 20 litres of water is added and the whole mixed and then left for six hours, after which it is passed to the filter-presses, about 80 kilos of hydrosulphite solution being obtained.

According to Ger. Pat. 162,912 (1904), crystallised hydrosulphite is obtained anhydrous and stable by adding to 1 vol. of saturated hydrosulphite solution, 3–4 vols. of 95 per cent. alcohol at 60–70°. The crystalline mass that separates is then dried in a vacuum. Treatment of concentrated hydrosulphite solution with concentrated sodium hydroxide (or NaCl or $CaCl_2$) solution at 50–70° also precipitates anhydrous hydrosulphite as powder, this being filtered off, washed with alcohol and dried in a vacuum; the alkaline mother-liquors (25–26% at 30°) deposit the residual hydrosulphite with $2H_2O$ on cooling (Ger. Pats. 171,991 of 1905 and 189,088 of 1906).

It is formed also on mixing a solution of a bisulphite with titanium chloride (Ti_2Cl_6), and then immediately pouring the whole into a solution of sodium hydroxide, thus precipitating titanium hydroxide, which can be recovered.

It is obtained electrolytically by using neutralised bisulphite as the cathodic liquid and a solution of sodium chloride as the anodic liquid, thus avoiding current losses due to secondary reactions (formation of thiosulphate: $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$). There are, however, difficulties in obtaining solutions stronger than 2·5 per cent., it being necessary to use high current densities or small cathodic volumes, the liquid being cooled and stirred, and good diaphragms used (*see also* Ger. Pat. 276,059 of 1912).

A very promising new process which leads directly to dry sodium hydrosulphite consists in treating metallic sodium with liquid or gaseous SO_2 in presence of petroleum ether, from which it is easily separated: $Na_2 + 2SO_2 = Na_2S_2O_4$. It may be made directly also by injecting liquid SO_2 into moist zinc dust, kept stirred; the zinc hydrosulphite formed is then decomposed with calcium hydroxide and the solution decanted from the insoluble zinc hydroxide, which may be sold for the preparation of zinc or its salts. The following constitution is now attributed to sodium hydrosulphite: $NaSO_2 . O . SONa$ (Binz, 1909).

In order to separate sodium hydrosulphite from its solutions, these are treated with salts (NaCl, $CaCl_2$, or $MgCl_2$, etc.), and the hydrosulphite is then pressed and washed with alcohol in order to eliminate all the water, and finally dried in a vacuum desiccator in the cold. It can be dried and rendered stable more economically and without much loss by placing it in ovens on hollow iron plates in which superheated steam circulates.

Stable compounds of hydrosulphites have been successfully prepared (since 1905) by combining them with formaldehyde: $Na_2S_2O_4, 2CH_2O, 4H_2O$. According to Bernthsen, these formaldehyde-hydrosulphites consist of an equimolecular mixture of $NaHSO_3, CH_2O, 2H_2O$ and $NaHSO_2, CH_2O, H_2O$. The latter is a derivative of sulphoxylic acid, H_2SO_2, being sodium formaldehyde-sulphoxylate, and may be separated by crystallisation from dilute methyl alcohol; it constitutes the active part of the discharging and reducing agents with a hydrosulphite basis, and is sold as *Rongalite*, BASF, while the above mixture bears the trade name of *Hydrosulphite* NS or *Hyraldite*. Bernthsen has obtained pure the following hydrosulphites: $Na_2S_2O_4, 2H_2O$; $K_2S_2O_4, 3H_2O$; $CaS_2O_4, 1\frac{1}{2}H_2O$, slightly soluble; ZnS_2O_4, readily soluble; $HNaSO_2, CH_2O$.

The reducing power of these hydrosulphite-formaldehyde compounds is increased by addition of zinc oxide or magnesium carbonate, or by reduction with zinc, etc. According to Blumberg and Rindskopf (Fr. Pat. 414,013, 1900), sulphoxylate-formaldehyde is obtained as follows: 100 parts of sodium bisulphite solution of 38° Bé. are mixed in an autoclave with 25 parts of 40 per cent. formaldehyde and 50 parts of zinc dust, the air being expelled by means of a current of CO_2; the autoclave is then closed, the mass stirred, and a pressure of 6–8 atmos. produced with CO_2. The temperature rises slowly to 40–50°, and after some hours the reaction is at an end.

Hydrosulphites are rendered more stable also by mixing them with salts of weak acids such as borates, basic phosphates, etc. (*see* Ger. Pats. 125,207, 129,861, 133,040, 141,452, 144,281, 144,632, 148,125, 162,875, 162,912, 172,217, 200,291, 203,910, 207,593, 213,586, 224,863, and 235,835; Fr. Pats. 341,718, 360,620, 401,000, 413,032 and 422,241; Eng. Pat. 20,580).

Solid sodium hydrosulphite now costs less than 2*s*. 6*d*. per kilo.

About twenty different hydrosulphite preparations for use in dyeing are on the market, containing aldehydes, zinc compounds, tin compounds, etc. (*rongalite, blankite, hyraldite, decroline*, etc.). For the reduction of indigo alone, without other vat dyestuffs (algol, indanthrene, etc.), it is calculated that 300 tons of these compounds are used annually in France.

SODIUM PYROSULPHITE (or metabisulphite), $Na_2S_2O_5$: *see* p. 584 and also the potassium salt, p. 544.

SODIUM PERSULPHATE: $Na_2S_2O_8$. This is prepared, as has been described in the section on persulphuric acid (p. 328), by electrolysing a solution of sodium sulphate in H_2SO_4 (Ger. Pat. 81,404) and gradually adding solid sodium carbonate to the cooled anodic chamber in order to neutralise the persulphuric acid that is formed.

POTASSIUM PERSULPHATE is also known, and is obtained by electrolysing a saturated solution of potassium bisulphate.

AMMONIUM PERSULPHATE, $(NH_4)_2S_2O_8$, is of more importance, and is formed by electrolysing a saturated solution of ammonium sulphate at 7°, when it separates as a solid. In general the current density per unit surface of the electrodes should be rather high. According to the patents (Ger. Pats. 155,805, 170,311, 173,977 and 205,069) good results are obtained by the electrolysis of sulphates even without diaphragms, by adding small quantities of fluorides. Ammonium persulphate dissolves in twice its own weight of water. When dissolved in sulphuric acid it forms *Caro's reagent* (*see* p. 329). Pure crystallised ammonium persulphate costs about 2*s*. 10*d*. per kilo.

APPLICATIONS. The persulphates are used for bleaching soap and for deodorising whale and seal oils and fish oils and stearines in general, so that they may be used in soap-making. In 1910 Switzerland alone manufactured 100 tons of persulphates.

SODIUM SULPHIDE: Na_2S, and **SODIUM HYDROSULPHIDE**: NaSH. These compounds are similar to the potassium compounds and are used in place of them, being cheaper. Sodium sulphide is used, for instance, in dyeing cotton with sulphur dyestuffs, in the manufacture of dyestuffs, in tanning for dehairing hides, for cleaning cotton, silk, etc., and, containing much dissolved sulphur, as an insecticide, especially against locusts.

Industrially it is prepared by melting a mixture of anhydrous sodium sulphate and coke in a flame furnace (similar to those used for HCl, p. 173), the hearth being made of basic stone in order to prevent explosions. A very fluid mass is first formed with flames of CO bursting from it, so that the atmosphere is always free from oxygen; the mass becomes denser and is then discharged and allowed to set, the reddish blocks obtained being broken and lixiviated—as with Leblanc soda (*see* p. 593)—and the decanted solution concentrated to crystallisation. Bollo and Cadenaccio (Fr. Pat. 423,228, 1910) complete the reaction at a lower temperature and more rapidly by adding oxides of iron to the fused mass.

A serious difficulty in the fusion is the ease with which the sulphide undergoes oxidation to sulphate; this may occur at any temperature, but is avoided by addition of a little barium sulphide, which with the sodium sulphate yields barium sulphate and sodium sulphide. When hopper furnaces are used, an air-jet is applied at a zone some little distance from the bottom, where the fused sodium sulphide accumulates as it is formed and whence it is run off. The proper temperature is easily attained if very dry sawdust is mixed with the powdered sodium and barium sulphates and sodium bisulphate and the mass made into blocks, with which the furnace is charged. Into the fused sulphide discharged from the furnace (still containing barium sulphide) branches of green trees are plunged, these undergoing charring with evolution of CO_2; the solid sulphide is thus rendered spongy and is easily broken before lixiviation.

Reverberatory furnaces have likewise been tried, but without practical success; also electric furnaces do not give good results, except for the preparation of barium sulphide, which, with sodium sulphate, gives sodium sulphide (somewhat impure).

Sodium sulphide is prepared on a large scale by heating sodium bisulphate (best mixed with the sulphate) with sodium chloride and coal to above 950°:

$$NaHSO_4 + NaCl + 2C = Na_2S + HCl + 2CO_2.$$

The bisulphate, which is an almost valueless by-product in the manufacture of nitric acid, can thus be utilised.

Sodium sulphide is soluble, but the sulphate insoluble, in alcohol.

The pure sulphide is prepared from the aqueous solution in octahedra: $Na_2S + 9H_2O$ (32 per cent. Na_2S). It is also sold in the fused almost anhydrous condition (65 per cent. Na_2S), as in this form it costs less to transport and also keeps better. The aqueous solution has a strongly alkaline reaction (p. 272). The crystallised sulphide for industrial use costs £8 per ton, the anhydrous product £12, and the fused product often £26. Germany exported 6600 tons of sodium sulphide in 1905 at £6 16*s*. per ton; in 1908 it exported 6536 tons, in 1909 7600 tons, and in 1913 8200 tons. In 1913 Austria exported 200 tons.

Italy produced 140 tons in 1905, 450 in 1906, 486 in 1907, 584 in 1909, 400 in 1911, 755 in 1913, 2089 in 1914, and 1654 (£27,900) in 1915; the importation into Italy amounted to 667 tons in 1908, 1658 in 1910, 1173 in 1912, and 1511 in 1913. In France 1500 tons were consumed in 1900 (prior to the use of sulphur dyestuffs), whilst in 1913 2500 tons of the fused sulphide and 5000 tons in crystals ($Na_2S + 9H_2O$) were consumed.

Analysis of Sodium Sulphide. The strength is determined by means of $\frac{N}{10}$ iodine solution after first acidifying with acetic acid) in presence of starch paste (1 c.c. of $\frac{N}{10}$ iodine corresponds with 0·0039 grm. of Na_2S).

The titration may also be carried out very exactly, even in presence of hydrosulphites or other impurities, by first acidifying the solution of Na_2S slightly with acetic acid and then titrating it with a standard solution of zinc sulphate; the end of the precipitation of zinc sulphide is found by spotting it on to paper containing cadmium sulphate, unti' this no longer gives a yellow spot.

The *hydrosulphide* is obtained from the calcium sulphide of Leblanc soda residues, by treating it in the cold with sodium bisulphate:

$$CaS + NaHSO_4 = CaSO_4 + NaSH.$$

The hydrosulphide is decomposed on boiling in the following manner:

$$2NaSH = Na_2S + SH_2.$$

Various *polysulphides*, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5, are also known; the last is obtained by adding sodium to pure sulphur.

SODIUM CARBONATE: Na_2CO_3 (SODA)

On account of its wide application, this is certainly the most important of the salts of the alkali metals from an industrial standpoint.

It is found in nature in certain rocks and is dissolved from them by rain water, which carries it into alkaline mineral springs (Vichy, Carlsbad, etc.). Certain supplies of such water collect in basins forming lakes in Egypt, America, etc., which by slow and spontaneous evaporation deposit a salt of the formula: Na_2CO_3, $CO_3HNa + 3H_2O$, which is called *Urao*[1] in Colombia and *Tro-na* in Egypt. From the lakes of California, and especially of Inyo County, large quantities of soda are obtained by simple crystallisation. The natural soda of Lake Magadé near Kiu in Uganda apparently forms a deposit of 200,000,000 tons, and in 1911–1912 an English company was formed to develop it; it is profitably sold in China and Japan.

Before the invention of the Leblanc process soda was extracted from the ashes of marine plants (*Chenopodium*, *Salicornia*, *Atriplex*, *Salsola*, etc.); in Southern France and Spain such plants are still specially cultivated in order to obtain soda and other products from their ash. Almost all soda is, however, to-day prepared by chemical means, starting from sodium chloride, which is treated according to one of the two methods described below.

PROPERTIES. Soda is a white substance of varying crystalline character according to the quantity of water of crystallisation which it contains. On slowly cooling an almost saturated solution of soda of 32° Bé., large crystals with 10 mols. of water, $Na_2CO_3 + 10H_2O$ (63 per cent. of water), are obtained, forming monoclinic prisms of common *soda crystals*; these effloresce in the air, forming a white powder of $Na_2CO_3 + H_2O$.

Soda crystals melt in their water of crystallisation at 32·5°, forming a saturated solution of this hydrate, but at a more elevated temperature another hydrate, $Na_2CO_3 + 2H_2O$, separates as a powder, which loses a further molecule of water in the air, forming another fairly stable hydrate, $Na_2CO_3 + H_2O$, which only loses the final molecule of water at 100°, forming anhydrous soda,[2] which has the specific heat 0·250.

Other hydrates are also known and they all have their own solubility curves. The anhydrous carbonate easily absorbs moisture from the air, up to 15 per cent., without becoming deliquescent, differing in this way from potassium carbonate. It melts at 850°, losing a small quantity of CO_2, and volatilises at very high temperatures. 100 parts of water at 20° dissolve 7 parts of anhydrous soda, at 10° 12, at 15° 16, at 20° 21·7, at 25° 28·5, at 30° 37·2, at 37° 59·5, at 38° 51·67, and at 100° only 45·1 parts (*see* Table); thus, soda behaves similarly to sodium sulphate.

---

[1] It contains various impurities (sand, clay, insoluble organic matter, sodium sulphate and some sodium chloride), these being eliminated by treating the powdered mass with a solution of crude urao, which dissolves almost exclusively NaCl (up to 15 per cent.), together with a little Na_2SO_4 and practically no soda. Part of the residue is dissolved and the solution used for dissolving out the sulphate from the remainder of the residue, the mass being then washed with soda solution, compressed into cakes which are dried in the air and heated in furnaces to about 600° to destroy organic matter. They are then dissolved in water and the solution filtered and concentrated until the soda, in a fairly pure condition, crystallises out (Ger. Pat. 143,447, 1902). The soda of the lakes of Algeria and in general of the northern Sahara contains also $MgCl_2$, $CaCO_3$, and $CaSO_4$.

[2] Soda may be obtained in very fine crystals by forcing a concentrated solution heated to 35° through a pulveriser (kept hot with steam) and passing the fine spray down a pipe up which cold air passes rapidly, the soda being thus solidified and the falling crystals subdivided (Ger. Pats. 124,405 of 1900 and 267,004 of 1912).

In aqueous solution it has a strongly alkaline reaction, for the same reasons as were explained in the case of potash. All acids liberate carbon dioxide from soda.

We give a Table below showing the densities and concentrations of solutions of sodium and potassium carbonates. We shall now explain in some detail the various industrial processes used for the preparation of soda, which constitutes one of the most important products supplied by modern chemical industry.

SPECIFIC GRAVITIES AND CONCENTRATIONS OF SOLUTIONS OF SODIUM AND POTASSIUM CARBONATES

Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of K_2CO_3	Per cent. by weight of Na_2CO_3	Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of K_2CO_3	Per cent. by weight of Na_2CO_3 at temp. of 30°
1·007	1	0·7	0·67	1·231	27	23·5	21·42
1·014	2	1·5	1·33	1·241	28	24·5	22·29
1·022	3	2·3	2·09	1·252	29	25·5	23·25
1·029	4	3·1	2·76	1·263	30	26·6	24·18
1·037	5	4·0	3·43	1·274	31	27·5	25·11
1·045	6	4·9	4·29	1·285	32	28·5	26·04
1·052	7	5·7	4·94	1·297	33	29·6	27·06
1·060	8	6·5	5·71	1·303	34	30·7	27·97
1·067	9	7·3	6·37	1·320	35	31·6	(59·5 per cent. at temp. of 37·5°)
1·075	10	8·1	7·12	1·332	36	32·7	
1·083	11	9·0	7·88	1·345	37	33·8	41·1 at 100°
1·091	12	9·8	8·62	1·357	38	34·8	
1·100	13	10·7	9·43	1·370	39	35·9	
1·108	14	11·6	10·19	1·383	40	37·0	
1·116	15	12·4	10·95	1·397	41	38·2	
1·125	16	13·3	11·81	1·410	42	39·3	
1·134	17	14·2	12·43	1·424	43	40·5	
1·142	18	15·0	13·16	1·438	44	41·7	
			at temp. of 30°				
1·152	19	16·0	14·64	1·453	45	42·8	
1·162	20	17·0	15·49	1·468	46	44·0	
1·172	21	18·0	16·27	1·483	47	45·2	
1·180	22	18·8	17·04	1·498	48	46·5	
1·190	23	19·7	17·90	1·514	49	47·7	
1·200	24	20·7	18·76	1·530	50	49·9	
1·210	25	21·6	19·61	1·546	51	50·1	
1·220	26	22·5	20·47	1·563	52	51·3	

I. LEBLANC PROCESS. This is the older process,[1] and is based on

---

[1] The origin of the soda industry may be traced back to the eighteenth century. In 1736 Duhamel showed that sodium chloride and natural soda contain the same base, and indicated that it should therefore be possible to transform salt into soda. In 1776 Scheele showed that on heating a solution of sodium chloride with lead oxide and then passing carbon dioxide into the filtered liquid, soda was obtained. This process was patented by Turner in 1787. In 1775 the French Academy awarded a prize to the work of Malherbe and De la Metherie, who succeeded in preparing soda in the laboratory by heating Glauber's salt (sodium sulphate) with carbon. Attempts to manufacture soda on a large scale by this process failed completely. Nicola Leblanc (1742–1806) first devised a complete process for transforming sodium chloride into the carbonate by way of sodium sulphate. In laboratory experiments he transformed sodium sulphate easily and directly into the carbonate by heating it with carbon and calcium carbonate, and in 1783 he obtained a prize from the Academy for his process. Leblanc, who was the medical man of the Duke of Orleans, obtained from the latter £8000 in order to construct the first soda-works

the transformation of sodium chloride into sodium sulphate in the manner which we have already described in connection with the manufacture of hydrochloric acid (p. 173).

The crude sulphate is then mixed with an excess of coal and calcium carbonate and the whole was formerly heated to redness in reverberatory furnaces somewhat different from those shown on p. 173. Now, however, revolving furnaces, consisting of large cylinders revolving on their axes and continuously traversed by the flame from a neighbouring hearth, are used. Rotary furnaces for the production of large quantities, which give good results, are constructed, for instance, at the works of Carrick and Wardale in Gateshead (Fig. 234).

The mixture of sulphate, limestone, and coal is introduced into the rotary cylinder, *B′*, which consists of a large wrought-iron cylinder lined with refractory bricks, 6 to 8 metres long and 2½ to 3½ metres in diameter, holding 15 to 20 tons of the mixture, four charges of which are treated per day. The cylinder revolves on four wheels, *C*, through the action of the cog-wheel, *I*. The flames and hot gases from the furnace, *D*, enter through the mouth, *E*, which is joined to the cylinder by means of a ring, affording a sufficiently close joint, although it allows the cylinder to revolve. The very hot gases which escape at the outlet, *F*, pass over the surface of soda solution from previous operations, this being contained in the pan, *G*, and thus evaporated.

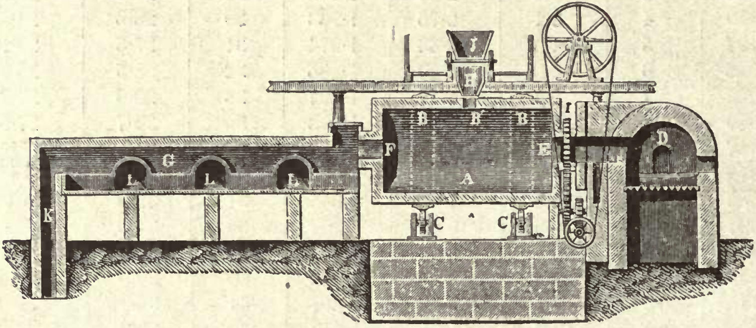


FIG. 234.

In practice 100 kilos of sodium sulphate from the pan, which should not be melted to a compact mass but should be porous, is used in lumps as they are obtained from the salt-cake pans and mixed coarsely by hand with shovels, or by rapid mechanical mixers, with 80 to 90 kilos of crushed limestone or chalk containing little magnesia, iron and silica,

---

at St. Denis in 1781, but in 1793, when the Duke of Orleans was guillotined, the St. Denis works were closed, and the Committee of Public Safety obliged Leblanc to make his secret public in order to replace potash by soda for the national requirements, as potash could not be obtained on account of the commercial isolation of France. As compensation they then made over the works of the Duke of Orleans to Leblanc, but he no longer had the means to work a factory on such a large scale, and became extremely poor. In 1806 he retired into an almshouse, where, as a last resource in his great misery, he committed suicide. In France he was only recognised much later, after hundreds of millions of tons of alkali had been industrially prepared in England and Germany by the Leblanc process, and it is only of late years that his countrymen thought of erecting a monument to their unfortunate fellow-citizen. The manufacture of soda had already been attempted by Losk in England, who could not obtain a footing until the enormous taxes which were levied on salt were reduced. The large works of Muspratt in England (1824) almost presented the soda to their customers in order to show that it had a value at least equal to natural soda. From that time this industry extended, especially in England, and underwent great improvements in mechanical directions, whilst, on the other hand, from a chemical standpoint the prescriptions of Leblanc were almost exactly followed. The more important improvements were that of Gossage, who in 1836 introduced the coke tower for absorbing HCl (*see* note on p. 175); and that of Stevenson and Williamson, who devised rotary soda furnaces, and then the systematic lixiviation and the mechanical calcining furnace. Later, through the assiduous work and repeated experiments of Schaffner, Mond, and Chance, it became possible to utilise the enormous quantities of sulphur which were formerly lost, and are still in large part lost to-day, in the alkali waste.

and 40 to 50 kilos of small coal. The coal should contain little ash, always less than 10 per cent., and more especially very little silica, as this causes loss of soda in the form of soluble silicates or may even form other insoluble mixed silicates; if it contains much nitrogen the coal forms cyanides and thiocyanates which render the soda impure.

When the operation is almost finished a further 6 to 7 per cent. of sulphate and a little powdered limestone are added; the mass then becomes more liquid and is easily discharged through the opening, *B′*, when this is turned downwards, into suitable cars arranged under the furnace. The fused mass solidifies, and becomes spongy and friable after some days under the influence of atmospheric moisture.

In the furnaces the two following reactions occur:

(*a*) $SO_4Na_2 + 2C = Na_2S + 2CO_2$ and $SO_4Na_2 + 4C = Na_2S + 4CO$
(*b*) $Na_2S + CaCO_3 = CaS + CO_3Na_2$.

The end of the reaction is indicated by the appearance of bluish flames of CO, as a portion of the $CaCO_3$ is decomposed into $CaO + CO_2$, and the CO_2 in presence of carbon is in turn converted at that temperature into CO: $CO_2 + C = 2CO$.

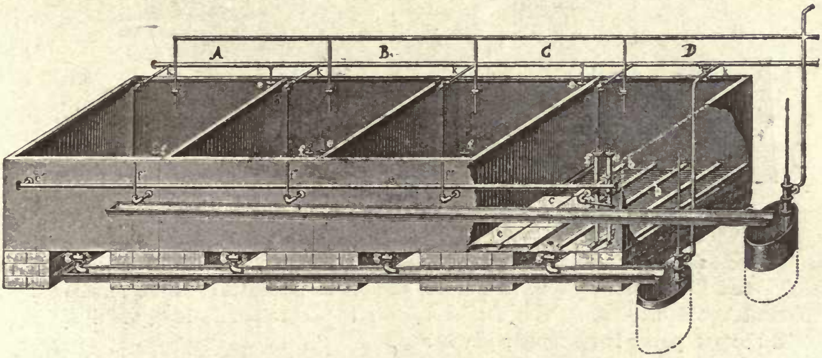


FIG. 235.

The *black ash* thus obtained consists of a mixture of sodium carbonate, excess of calcium carbonate, sodium sulphide, excess of coal, calcium oxide, and other impurities. After cooling, the black ash is systematically lixiviated with cold water in a suitable plant, and since the liquid becomes hot the temperature is lowered as far as possible to 40° or 50°, as in this way less highly coloured solutions are obtained and the formation of sodium hydroxide is avoided (*see below*).

For this purpose use is made of several iron tanks with perforated double bottoms, arranged in series (Fig. 235). The bottom is covered with a thin layer of cinders, and then each vat is filled with lumps of black ash, and water is passed into the vat *A*. A pipe dips down to the bottom of this vat and carries the solution into the upper part of the vat *B*, and in the same way the solution passes from *B* to *C* and from *C* to *D*. The solution in *D* should be of 28° to 30° Bé.; if it is more concentrated it dissolves more sulphide and iron salts which colour the solution deeply. On then lowering the tube *f′* into the vat *D*, the solution is discharged into channels, *i*, which carry it into a tank from which it is pumped into the evaporating pans. The soda in *A* will be the first to dissolve completely; the muddy residue is then discharged from the cock, *g*, at the base, and after thoroughly rinsing with water, this vat is filled with fresh crude soda. At this point the solution which passes into the last vat, *D*, instead of being discharged, is passed through the tube *e* into the first vat, *A*, where it becomes saturated and is then discharged through the tube *f*; the vat *B*, which remains empty, is next filled as was done for *A*, and *B* becomes the last vat to be discharged, and so on in such manner as to obtain a rational, systematic, and continuous lixiviation.

The whole of the impurities, consisting of calcium sulphide, calcium carbonate, coal, and a certain quantity of other impurities, form the so-called *alkali waste*. It must be borne in mind that during lixiviation the calcium oxide reacts with the soda, forming insoluble calcium carbonate and soluble sodium hydroxide:

$$CaO + H_2O + CO_3Na_2 = CaCO_3 + 2NaOH.$$

For this reason, amongst others, a works manufacturing sodium carbonate always manufactures sodium hydroxide as well. In fact, if an excess of coal is added in the black ash furnace, and this is heated to higher temperatures and the crude soda lixiviated with hot water, more sodium hydroxide than sodium carbonate may be formed.

When the production of carbonate alone is required, the small amount of hydroxide present in the solution obtained on lixiviation must be transformed into carbonate by passing a current of air and carbon dioxide through the solution. This process is called *carbonating*, and chimney gases are commonly used; by this means the small amounts of dissolved calcium sulphide and sodium sulphide which are present are oxidised, forming sulphates, and the alumina, iron, and silica present as impurities in the solution are precipitated at the same time. The completion of this reaction is recognised by the fact that lead acetate paper is no longer blackened.

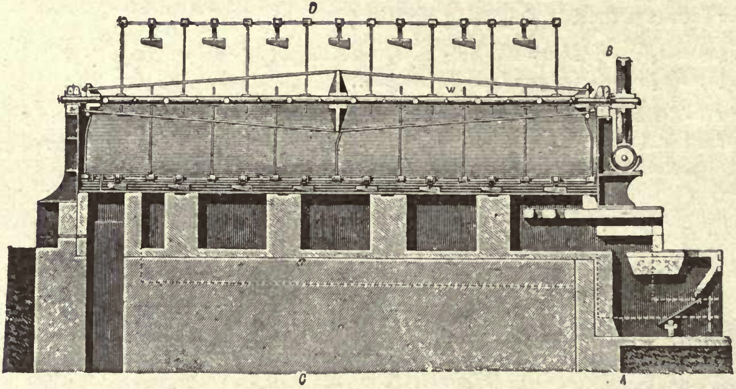


FIG. 236.

On standing, a clear solution of sodium carbonate is obtained, this being then decanted and evaporated. When a certain concentration has been acquired, crystals of sodium carbonate, $Na_2CO_3 + H_2O$ (*black salt*), separate from the hot liquor, and are gradually removed, whilst new solution is added to the liquor in the pans; thus the process becomes continuous.

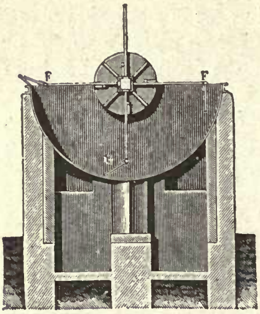


FIG. 237.

For this purpose use is made of long, narrow, round-bottomed pans, heated by direct flame, and so arranged that the lower part of the bottom rests on the brickwork of the hearth, and is not directly heated by the flame, so that the salt which separates is not burnt.

To-day, however, Thelen's open pans, heated by direct flame, are generally employed; these are provided with an automatic stirrer, and the pure carbonate which separates on evaporation is automatically discharged. Fig. 236 represents a longitudinal section, and we see how the inclination of the scrapers on the stirrer causes all the crystals to pass to one extremity of the pan, whence they may be removed by a suitable elevator. Fig. 237 shows a transverse section of the same pan, and shows still more clearly the movement of the scrapers, which are somewhat loose.

The highly concentrated mother-liquors are discharged at intervals and contain sodium ferrocyanide and other impurities together with soda. These mother-liquors are finally concentrated apart and the residue calcined, impure soda ash being thus obtained.

The black salt which is first obtained is separated from the mother-liquors in a hydro-extractor; if the soda has been previously carbonated it is then calcined in ordinary reverberatory furnaces and not in cylindrical rotary furnaces, because it would there melt, in which case it would be necessary to work it up again. If carbonisation and oxidation have not been completed the soda is mixed with sawdust and charged into reverberatory furnaces for calcination. It is important to regulate the temperature in such a manner that the soda does not melt, as otherwise it becomes unusable, and it must also be kept continually moving so that all the sawdust may be converted into carbon dioxide, which forms carbonate with the NaOH.

For this purpose rotary calcining furnaces are constructed; a much-used form is that of Mactear, which is able to produce 100 tons of calcined soda ash per week.

An iron platform (Fig. 238) 6 to 7 metres in diameter (2) is mounted on wheels (3) and is covered by refractory material (1); its extreme rim is provided all round with a small channel (51) in which molten soda forms a seal with the vault of the furnace (6, 7, and 23), supported by a suitable iron framework. Under the periphery of the platform is a cogwheel which enables the whole platform to be revolved by means of the spur-wheels (50). The soda to be calcined is charged through the central aperture (18), and is finally discharged through the central opening (19). During the circular movement hot gases and flame pass in from the hearth (9), and the mass of soda is continuously stirred up by a system of agitators (22) fixed in the roof of the furnace and actuated by cogwheels. The soda obtained from these furnaces is already sufficiently pure for many industrial purposes. If a purer crystalline soda is required it is dissolved in suitable vats and a little chloride of lime is then added in order to oxidise and precipitate the various impurities (iron, alumina, etc.). The clear, decanted or filtered solution is evaporated in ordinary pans, for example, Thelen pans (*see above*).

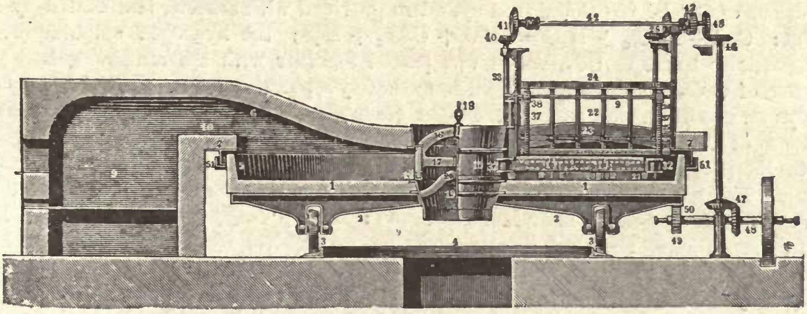


FIG. 238.

The refined soda crystals which are thus obtained are calcined in a well-cleaned ordinary furnace, after which they are ready for sale; they are usually packed in sacks, on which their strength in soda is marked.

If large transparent soda crystals are required the concentrated hot solution is allowed to cool slowly in suitable vats; the soda crystals of commerce are of the composition, $Na_2CO_3 + 10H_2O$, thus obtained; these are still wrongly preferred in some quarters to calcined soda, although they contain 63 per cent. of water.

In order to be able to meet the competition of the Solvay process (Ammonia Process, *see below*), it is necessary in using the Leblanc process to utilise all the by-products as far as possible; thus, the HCl formed in the manufacture of the sodium sulphate must be used for the preparation of chlorine or bleaching powder, and the sulphur contained in the alkali waste (consisting of about 40 per cent. of CaS, 22 per cent. of $CaCO_3$, 3 per cent. of iron sulphide, 15 per cent. of sand and silicates, 4 per cent. of soda, 10 per cent. of lime, etc.), must also be utilised as far as possible. In spite, however, of the utilisation of the residues of the Leblanc process, the latter is now almost completely supplanted by the ammonia process.[1]

Until a few years ago (1900) this alkali waste, besides being a source of much loss of capital, as it contained 20 or 25 per cent. of sulphur, constituted a regular calamity for the

---

[1] D. Crispo (1909) maintains that, if suitable furnaces could be constructed, the manufacture of soda according to the equation, $Na_2SO_4 + C + SiO_2 = SiO_3Na_2 + SO_2 + CO$ and $SiO_3Na_2 + CaCO_3 = Na_2CO_3 + CaSiO_3$, could be attempted. Sometimes, however, much sodium polysilicate is formed, and this is not easily transformable.

industry and for the inhabitants of the neighbourhood of the works. A truly enormous bulk of material was thus obtained, because each ton of soda which was produced supplied 1½ tons of dry waste, and thus all this material collected in mountains which developed a smell of hydrogen sulphide through the action of the air, which was thus polluted, and water dissolved coloured and evil-smelling sulphides which passed into the soil and defiled the water of wells and rivers.

The treatment of alkali waste thus constituted a problem of capital importance both from the hygienic and financial standpoints: all the sulphur was lost in quantities which corresponded with about one-third of the weight of soda produced, England alone losing annually more than 150,000 tons of sulphur, of the value of about £400,000.

Numerous experiments were made and very important work was undertaken on this question, and after repeated failures, and after the hopes aroused by Schaffner in 1880 (he obtained calcium thiosulphate, CaS_2O_3, after many operations and then decomposed this with HCl, thus recovering sulphur and SO_2), the process had to be abandoned owing to the increased price of HCl, and to the fact that only 50 per cent. of the sulphur was recovered. Mond then attempted to solve the question, and finally the Schaffner-Helbig process arose, which reduced the sulphur losses to a minimum, at the same time recovering the calcium carbonate.

According to this system calcium sulphide was decomposed with magnesium chloride (solutions of 24° Bé.) in closed iron cylinders provided with stirrers, and heated by direct steam: $CaS + MgCl_2 + H_2O = MgO + CaCl_2 + H_2S$; the hydrogen sulphide evolved was partially burnt to SO_2, which was passed together with the remaining H_2S into a solution of $CaCl_2$, all the sulphur then immediately separating: $SO_2 + 2H_2S = 2H_2O + S_3$, always on condition that exactly the right proportions of H_2S and SO_2 were present. In presence of $CaCl_2$ the sulphur separated in lumps and was thus easily filtered.

On then passing a current of carbon dioxide into the mixture of $CaCl_2$ and MgO resulting from the first reaction, magnesium chloride and calcium carbonate were formed; the latter was then again used in the manufacture of soda: $MgO + CaCl_2 + CO_2 = CO_3Ca + MgCl_2$.

In 1888 Chance rendered the process more economical by perfecting the process of Gossage (1838) by which CaS was decomposed with CO_2 and H_2O, and the H_2S formed completely burnt, forming SO_2, which was used for the manufacture of sulphuric acid. Chance found it more remunerative to burn the hydrogen sulphide partially in such a manner that the H only was transformed into H_2O, while all the sulphur was separated as such: $H_2S + O = H_2O + S$ (*see* p. 218).

The important point in this process is to employ exactly the right proportions by volume of H_2S and air. The process is remunerative, but requires very costly plant.

To-day the method of Chance, modified by Claus, is everywhere employed. A current of carbon dioxide (chimney gases) is passed into the residues in aqueous suspension: $CaS + CO_2 + H_2O = CaCO_3 + H_2S$, and the hydrogen sulphide evolved is collected in large gasometers and then burnt with an insufficient quantity of air; the sulphur is then separated (regenerated sulphur) or is burnt with excess of air, thus forming SO_2, which is utilised in lead chambers for the manufacture of sulphuric acid.

It is estimated that by this process about 80,000 tons of sulphur are obtained annually in Europe. Since 1904 the United Alkali Company in Liverpool has transformed H_2S and SO_2 into sulphuric acid with a yield of 90 per cent. by passing these gases over a platinum catalyser at 538°.

II. AMMONIA SODA PROCESS (or SOLVAY PROCESS). This process was proposed by Dyar and Hemming as early as 1838, but was rendered industrially effective after many failures by the brothers Solvay in 1863.[1]

---

[1] It appears that Vogel in 1822 was already aware of the reaction by which soda is obtained by the ammonia process, and it is said that J. Thom in 1836 manufactured 100 kilos per day, but the first patent is that of Dyar and Hemming, of June 30, 1838. However, V. Ravizza showed by documents at a meeting of the Chemical Society of Milan in February 1910 that the Milanese pharmacist Gerolamo Forni on March 6, 1836, offered a project to the Austrian Government for the manufacture of 250 tons of soda annually by the ammonia process.

The first Solvay soda factory was erected at Couillet (near Charleroi) in 1863, and in 1910 this factory employed 430 operatives. Later a large works was erected at Dombasel (France), the number of workpeople before the war being 1200; the Salin-Giraud (France) works had 450 employees. Factories were started later in Germany, England, America, Russia, Austria, This is based on the reaction which occurs at ordinary temperatures between a solution of sodium chloride and one of ammonium bicarbonate, with formation of sodium bicarbonate:

$$CO_3HNH_4 + NaCl = NH_4Cl + CO_3HNa.$$

At high temperatures the reverse reaction may also occur. If the solution is concentrated the sodium bicarbonate, which is only slightly soluble, separates in the crystalline condition, whilst the ammonium chloride remains in solution.[1] On heating a solution of the bicarbonate, sodium carbonate is then easily obtained:

$$2CO_3HNa = CO_3Na_2 + CO_2 + H_2O.$$

The ammonia process cannot be employed for the preparation of potassium carbonate because the corresponding potassium bicarbonate is more soluble and does not separate in crystals.

Industrially the process starts from a cold saturated solution of NaCl; this is saturated with moist gaseous NH_3 in such a way that each litre of the solution contains 268 grms. of NaCl and 78 grms. of NH_3.

It is found in practice that in order to obtain a good yield it is necessary to employ about double the quantity of sodium chloride theoretically required; thus for 100 kilos of soda (99 per cent.) 210 to 220 kilos of salt are required, a part of which is lost (about 15 per cent.). (*Translator's note.*—This should be 50 per cent.)

The NaCl solution should not contain salts of calcium, magnesium, or iron, and in case these are present it is necessary to separate them with a little ammonium carbonate; this separation is not easy and is now effected economically by using the saturated salt solution first for washing the gases which escape from the apparatus in which the saturation with ammonia occurs; in this way about 1·2 per cent. of ammonium carbonate is introduced into the solution and complete saturation with ammonia is only carried out after the carbonates of calcium, magnesium, iron, etc., have been separated.

The saturated solution containing about 26 to 27 per cent. of NaCl is obtained by passing a current of water through vessels filled with salt and arranged in series. In a saturated solution of salt *dry* gaseous ammonia would precipitate NaCl because this is less soluble in an ammoniacal solution; when, however, *moist* NH_3 as it is regenerated from NH_4Cl is used, NaCl is not precipitated, because this carries with it sufficient moisture to dilute the solution, which at the end of this operation should still be saturated with salt. The original salt solution has a density of 23° to 24° Bé., and after saturation with ammonia a density of only 16° Bé., so that the volume is increased and each litre contains 60 to

---

Bosnia, Bolivia, Transylvania, and one at Torrelavega (Spain), combined with a salt-works and a coal-mine.

Even prior to 1880, Mallet and Boulouvard succeeded in working the ammonia soda process on an industrial scale (Fr. Pats. 94,213, 114,851, and 125,635), the salt being dissolved in aqueous ammonia and special 3-cylinder presses for pressing the sodium bicarbonate and a good carbonation apparatus being used. In 1878 they worked a factory at Sorgnes (near Avignon) with a daily production of 10 tons of soda, the plant costing £40,000 (a Solvay plant costing £50,000 gives up to 20 to 25 tons per day); a large profit was made for some years in spite of the disadvantageous position of the site for obtaining supplies of sodium chloride. An identical works was erected in 1883 at La Madeleine (near Lille) and then one at Salindres (Péchiney & Co.); the factory at Monfalcone (near Trieste) (*see later*) and that at Plumbley (England) perhaps worked on the same system. In the early days, 75 per cent. of the salt was utilised and 1¼ equivalents of limestone with a loss of 3·75 kilos of ammonium sulphate per 100 kilos of soda; the labour required, especially for the calcination, was, however, excessive.

[1] According to W. Mason (1914), the reaction really takes place between ammonium carbonate and salt: $2NaCl + CO_3(NH_4)_2 = Na_2CO_3 + 2NH_4Cl$, and, indeed, in practice the carbonation occurs in two phases: in the first, about 80 per cent. of the ammonia is transformed into ammonium carbonate, and in the second, with new CO_2, the slightly soluble sodium bicarbonate is formed and separates. If ammonium bicarbonate were present in large quantities, this also would separate crystalline, since it too is only slightly soluble; such separation does not, however, take place. Further, if the reaction took place between ammonium bicarbonate and sodium chloride, considerable absorption of heat should occur, whereas in the Solvay carbonation column much heat is generated, just as when sodium bicarbonate is precipitated from a solution of the carbonate by means of CO_2.

70 grms. of ammonia. If fresh salt is added to resaturate the solution further impurities in the form of calcium and magnesium are introduced; in order to avoid this disadvantage, almost dry ammonia is to-day employed by preference to saturate the saturated salt solution. The saturation of the salt solution (brine) with ammonia may be carried out in any of the usual forms of column apparatus similar to those employed in the manufacture of alcohol, or in the Grüneberg apparatus (p. 358), by allowing the brine to fall into the column from above and passing the current of gaseous ammonia from below. Solvay, however, employs a saturator similar to that shown in Fig. 239.

The two vessels, *R* and *R′*, which contain the saturated salt solution are used alternately and are in communication above and below, through *p*, *p′*, *r*, *r′*, with a vertical cylinder, *A*, into which the ammonia passes through the tube *T*, terminating in a perforated funnel. The ammonia from the rectifying column is first cooled to 70° to 80° in large cast-iron coils cooled by cold water, after which the ammonia passes through the salt solution which is maintained in circulation by the agitator, *W*, in such a manner that it continuously enters and passes out of the vessel, *R* or *R′*. Since the solution tends to become heated it is necessary to cool it by passing cold water through the coil, *S*. The excess of ammonia passes out through the tube *T*, and is absorbed by a dilute solution of NaCl. When the solution in *R* is saturated with ammonia it is necessary to add a little powdered salt through the tube *V*, in order to saturate the solution also with NaCl; the stirring is then stopped and the solution is driven over into the conical cylinder, *D*, by compressed air. Here the impurities are allowed to settle and are separated by means of the valve tube *M*, whilst the clear solution passes out through the tube *U* and, together with that remaining in the vessel, *R* or *R′*, is continuously pumped into the carbonating apparatus, which is called the *absorber*.

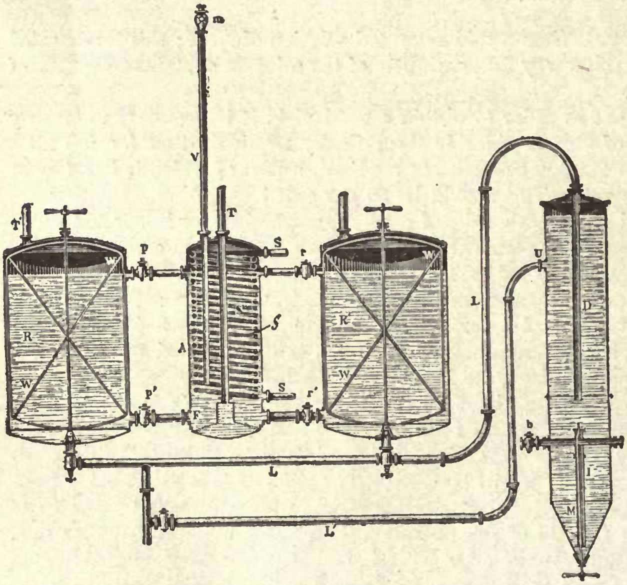


FIG. 239.

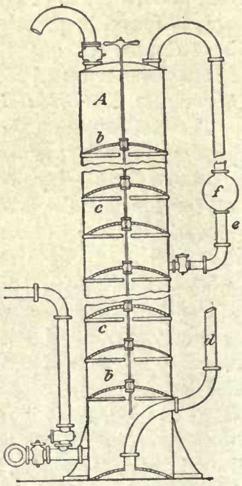


FIG. 240.

The absorber used by Solvay (Fig. 240) consists of a column formed of an iron cylinder 2 metres in diameter and 15 metres high, divided into a number of sections by means of perforated plates, *b*. The ammoniacal salt solution passes in through the tube *f*, which feeds several absorbers, and fills the columns up to a height of 12 metres. Compressed carbon dioxide passes in through the tube *d* at the base of the column and saturates the ammoniacal salt solution, forming insoluble sodium bicarbonate; the excess of CO_2, which carries with it a little ammonia, escapes at the top of the column and is conducted into the saturator containing salt solution (*see above*). The liquid mass, containing sodium bicarbonate in suspension, is filtered through vacuum filters in order to collect the bicarbonate, whilst the liquid, which contains ammonium chloride and free ammonia (60 grms. per litre), is mixed with milk of lime (200 grms. CaO per litre), and heated in the usual apparatus (pp. 357 *et seq.*) for the regeneration of all the ammonia.[1] Inside the Solvay column batteries of tubes in which cold water circulates are placed at various heights so that the whole mass is kept at a temperature below 40°. The best yield of bicarbonate is obtained at a temperature of 30° and with a pressure of about 2 atmos. in the column. More concentrated ammoniacal salt solutions give a better yield of bicarbonate and less loss of ammonia, but the bicarbonate is contaminated with NaCl and there is appreciable loss of salt.

A simpler type of absorber is that proposed by Honigmann and consisting of several iron cylinders with a conical bottom, united in series.

After these have been filled with ammoniacal salt solution a current of compressed carbon dioxide is passed through them successively, and when the contents of the first cylinder are saturated it is emptied and filled afresh. The CO_2 then first enters the second cylinder, which is not yet saturated, and passes through the successive cylinders and finally into the original first cylinder containing the fresh solution; the procedure is similar to that employed in systematic lixiviation (*see* above). During the saturation with CO_2 cold water is passed over the external surface of the cylinders in order to maintain the temperature at 30°. The complete carbonation lasts from 12 to 15 hours.

The carbon dioxide employed in this process is obtained by heating limestone ($CaCO_3$) in suitable lime-kilns (*see* Lime), arranged in layers alternately with gas coke containing little sulphur and arsenic (100 parts of limestone and 20 parts of coke). The carbon dioxide produced by the kilns is cooled and freed from dust and SO_2 by washing it in one of the ordinary towers with a counter-current of water.

The lime which remains in the kilns is used in the regeneration of ammonia from the ammonium chloride solutions.

The sodium bicarbonate which collects in compact cakes on the vacuum filters is sprinkled with a fine spray of water in order to free it from the last traces of mother-liquor. To transform it into carbonate it is calcined in reverberatory furnaces, or preferably in rotary furnaces or in pans with agitators similar to the Thelen pans (*see above*), but closed so that all the carbon dioxide developed during the heating may be recovered. The gases, containing 50 per cent. of CO_2, are cooled and washed and led through suitable pipes to the absorbers in order to be utilised directly in the formation of sodium bicarbonate. The soda ash which remains is dry, white and bulky, and contains 98 to 99 per cent. of Na_2CO_3.

As a by-product in the production of Solvay soda a solution of calcium chloride is obtained which Solvay has endeavoured to utilise by heating the solid residue of $CaCl_2$ obtained on evaporation with silica at a high temperature in a current of air. Free chlorine is thus obtained: $CaCl_2 + SiO_2 + O = CaSiO_3 + Cl_2$; this chlorine cannot, however, compete with electrolytic chlorine, and part of the liquid is now used only as brine in ice factories.

This process of treatment of calcium chloride is of no practical importance because electrolytic chlorine is now obtained at a very low price. Some works have found it profitable to treat the solution of $CaCl_2$ with sulphuric acid or sodium bisulphate; precipitated gypsum is thus obtained which can be used in various ways; after filtration a very dilute solution of HCl remains which may also be utilised in certain cases.

III. CRYOLITE PROCESS. Much soda is to-day obtained in North America and Denmark from a mineral which is very abundant in those countries and especially in Greenland, namely, *cryolite*, which is a double fluoride of aluminium and sodium, AlF_3, 3NaF. The finely powdered mineral is mixed with lime and heated in suitable furnaces. It thus forms insoluble calcium fluoride, which is utilised in glass and porcelain factories, and the double oxide of aluminium and sodium (sodium aluminate) which is soluble:

$$2(AlF_3, 3NaF) + 6CaO = 6CaF_2 + Al_2O_3, 3Na_2O \text{ (soluble).}$$

The mass is lixiviated with water and a current of carbon dioxide is passed through the solution, this precipitating aluminium hydroxide, which is utilised for the preparation of

---

[1] The liquid which is discharged from the apparatus after the recovery of the ammonia contains, per 100 c.c. of liquid, 1·4 grms. of CaO, 2 grms. of $CaCO_3$, 15 grms. of calcium and sodium chlorides, and 0·003 grm. of NH_3; this liquid is allowed to stand in order to recover the lime which separates.

alum, aluminium sulphate, or metallic aluminium, whilst a solution of sodium carbonate remains, which is concentrated in order to obtain solid soda:

$$Al_2O_3, 3Na_2O + 3H_2O + 3CO_2 = 3CO_3Na_2 + Al_2(OH)_6.$$

IV. ELECTROLYTIC PROCESS. When the principal difficulties in the preparation of electrolytic caustic soda had been overcome, the direct preparation of the carbonate from electrolytic soda by passing carbon dioxide into the cathodic zone, so obtaining crystallised sodium bicarbonate, was thought of; this could then be finally treated in the same way as that obtained in the Solvay process. The results of these attempts were kept secret, but many consider that this process could not be practical because the thermal balance of the chemical reactions passed through in order to obtain sodium carbonate in the ordinary way is more satisfactory than by the electrolytic process (*see above*), and in fact the commercial price of these products already expresses the difference in the thermochemical balance, and except in special cases it would not pay to transform electrolytic chlorine into HCl and electrolytic caustic soda into sodium carbonate.

APPLICATIONS. Soda is used in large quantities in the manufacture of soap and glass, in laundries, in the preparation and washing of textile fibres, in the manufacture of paper, in dyeing, and generally for the preparation of many sodium salts such as silicates, phosphates, dichromates, borax, etc.

The continuous fall in prices (*see later*) has enabled soda to be used in very many industries in which its use would not formerly have been thought possible; for instance, in building operations, by adding it to the mortar in order to be able to work in winter without fearing the action of the frost. A large palace at Brussels was actually constructed during a severe winter by preventing freezing of the mortar by the addition of soda. This fall in price has rendered it difficult, if not impossible, to start new works in competition with those which already exist, and which are being continually perfected.

In glass factories the replacement of sodium sulphate by sodium carbonate can be predicted when the latter is sufficiently cheap, as 3 kilos of soda produce the same effect as 4 kilos of the sulphate. It will have the advantage that the air of the neighbourhood will not be polluted with sulphur dioxide, and will also effect an economy in fuel and an increase in the output of the furnaces, which will also be less attacked and will produce glass of better quality.

STATISTICS AND TRADE IN SODA. For a long period England was the mistress of the world's trade in soda products in virtue of her powerful mercantile marine and large quantities of cheap fuel, and it was only much later that the soda industry was able to develop on the continent of Europe, especially after the introduction of the ammonia soda process. In 1876 £7,000,000 was invested in England in the soda industry, about 22,000 operatives being employed; in 1880 430,000 tons of soda were produced, almost all by the Leblanc process, although Ludwig Mond[1] started the first ammonia soda works in 1875. At present the proportion of English soda made by the Solvay process is more than 70 per cent., that of Continental soda being 90 per cent.

The Leblanc process would have been completely abandoned before now if enormous amounts of capital were not invested in the works using it and if the waste products (HCl and S) were not rationally utilised. These works are now being employed in making other products, especially as glass-makers are more and more replacing the sodium sulphate (from the Leblanc process) by sodium carbonate, which is now sold very cheap

---

[1] The English firm, Brunner, Mond & Co., with a capital of £3,000,000, has paid dividends as high as 100 per cent. and for a number of years continuously has paid 30 per cent. In 1891 it entered the English Soda Syndicate with forty-five works (United Alkali Company), with a capital of £8,800,000, which also paid high dividends; this capital was afterwards reduced. The Deutsche Solvay-Werke in Germany, with a capital of £2,000,000, made in 1904 a nett profit of £360,000, which has been maintained for some years. In Europe other ammonia soda works have been erected to compete with the Solvay works; these use more particularly the plant proposed by Honigmann.

and gives a better glass without contaminating the flue gases with SO_2. Some Leblanc soda works use solutions of the crude carbonate for making caustic soda by boiling with milk of lime (*see* p. 554).

PRODUCTION AND CONSUMPTION OF SODIUM CARBONATE (IN TONS)

Country		1882	1895	1900	1905	1910	1911	1912	1913	1914
England	prod.	450,000	800,000	—	—	—	700,000	—	—	—
	export.	—	—	—	—	121,000	138.000	—	—	—
Germany	prod.	90,000	—	280,000	350,000	—	400,000	—	—	—
	export.	—	—	40,500	47,000	60,000	—	—	—	—
United States	prod.	1,100	—	430,000	540,000	—	250,000	—	—	—
	export.	—	—	—	120,000	—	—	—	—	—
	import.	—	150,000	—	10,000	—	—	—	—	—
France	prod.	120,000	—	—	180,000	—	200,000	—	400,000	—
	export.	—	—	—	—	—	—	—	86,000	55,000
	import.	—	—	—	—	—	—	—	—	—
Italy	import.	—	—	24,000	29,600	45,174	45,596	49,285	— 52,339	48,115 53,191 (1915) 45,212 (1916)
Austria-Hungary	prod.	40,000	—	—	105,000	—	—	—	—	—
	export.	—	—	—	—	—	—	—	—	—
	import.	—	—	—	—	—	—	—	—	—
Russia	prod.	—	32,000	—	55,000	82,000	130,000	—	—	—
	import.	—	15,000	—	5,000	—	—	—	—	—
Belgium	prod.	8,000	—	—	34,000	—	—	—	—	—
Denmark	import.	—	—	—	—	—	—	11,855	—	—
World's production		700,000	1,280,000	1,650,000	1,800,000	2,100,000	—	—	3,500,000	—
Total Leblanc output		540,000	300,000	270,000	150,000	100,000	—	—	—	—

The world's consumption of soda (*see* Table), which in 1882 was 700,000 tons (only 160,000 tons being ammonia soda), has now reached about 3,500,000 tons, almost entirely ammonia soda (two-thirds made by the Solvay companies of various countries). North America produced only 1100 tons in 1886 and Germany 42,000 tons in 1878.

Before 1897 Russia imported almost all its soda, but now manufactures it, and since 1910 importation has ceased.

Italy does not produce sodium carbonate, and the small quantities figuring in the statistics (*e. g.*, 2435 tons in 1914) must be Solvay soda dissolved and crystallised. That imported prior to 1914 was supplied one-half from France, one-fifth from Germany, one-fifth from England, and one-tenth from Belgium. France produced 57,000 tons of soda in 1873 and 120,000 in 1882 (*see* Table). In 1915 France exported only 11,500 tons, and in 1916 26,850 tons.

Imports of soda to Spain were valued at £52,000 in 1910, and those to Brazil at £50,000; the Argentine imports were 9000 tons in 1910 and 8500 of anhydrous and 3500 tons of crystals in 1911.

The continuous fall in the price has greatly contributed to the large increase in the consumption of soda; thus in England, where crystallised soda containing 63 per cent. of water was sold at £10 per ton in 1840, the price had fallen in 1860 to £5 12*s.*, in 1870 to £4, in 1880 to £3 9*s.* 6*d.*, and in 1890 to £2. In Italy before the European War it was sold at £2 8*s.* per ton and calcined ammonia soda at £4 per ton, these prices being for large parcels delivered at Genoa from Great Britain or France. During the European War speculators raised the price to £80 per ton, while Messrs. Solvay sold it in France at £6 8*s.* to £7 4*s.* per ton and in Italy at about £10, but the little that arrived was requisitioned by the Government, who sold it to manufacturers at very high prices.[1]

---

[1] Before the European War the competitors in the Italian soda market were the Solvay companies of France, Belgium, and England on the one hand, and the Austrian works, especially that of Monfalcone, which dominates the Adriatic Sea, on the other. As a result of this competition, 98 per cent. ammonia soda was sold at £3 8*s.* to £3 12*s.* per ton. To overcome it, Messrs. Solvay erected a large works at Castiglioncello, near Leghorn, using as raw material a saturated rock-salt solution supplied to the works through pipes from borings in a neighbouring rock-salt deposit. In spite of the great scarcity of soda in Italy, this large factory, which was to cost more than £400,000, could not be finished before or during the war, owing to the difficulty of transporting large machines from America. During the war the factory was utilised to make caustic soda for France, whence sodium carbonate was sent to Castiglioncello to be treated with lime (*see* p. 554); part of this caustic soda was placed on the Italian market. When Italy entered the European War in 1915 against Austria, the Monfalcone factory was destroyed.

The strength of soda is commercially indicated by degrees which have various values in different countries. *German degrees* indicate the percentage of Na_2CO_3; *Gay-Lussac degrees* the percentage of Na_2O; *Descroizilles degrees* (French) the quantity of H_2SO_4 neutralised by 100 parts of the soda; *Newcastle degrees* (English) differ very little from Gay-Lussac degrees: actually 1° Gay-Lussac = 1·71° German = 1·58° Descroizilles = 1·01° Newcastle.[1]

SODIUM BICARBONATE : NaHCO (Sodium Hydrogen Carbonate, Primary Sodium Carbonate).

This substance is formed on passing a current of CO_2 and steam over soda maintained at a temperature of 80°: $CO_3Na_2 + CO_2 + H_2O = 2CO_3HNa$, or by passing CO_2 into concentrated soda solution.

It is obtained industrially in the manner already described as the first product in the manufacture of ammonia soda, but in this case it always retains small quantities of ammoniacal salts, and must therefore be recrystallised from water for certain purposes. It crystallises without water of crystallisation in small monoclinic tablets soluble in 10 parts of water in the cold, and the solution has a faint alkaline reaction. The dry salt decomposes even below 100°, forming CO_2. On boiling the solution a portion only of the CO_2 is first evolved, forming sodium sesquicarbonate, $CO_3Na + CO_3HNa + 2H_2O$, which is identical with the *Tro-na* of the Egyptian lakes, and on continuing the evaporation further CO_2 is evolved and the carbonate alone remains: $2NaHCO_3 = CO_2 + H_2O + CO_3Na_2$.

Sodium bicarbonate is used for the washing of silk and wool of fine quality; also in medicine and in the preparation of effervescing drinks. The crude commercial product costs about £8 per ton and when refined £10 per ton, whilst the chemically pure product costs £16 16*s*. In 1904 Italy imported 1530 tons, of the value of £12,240, in 1908 1308 tons (from England), in 1909 1707, in 1911 1578, in 1913 1369, in 1915 1150, and in 1916 1670 tons. England exported 23,000 tons in 1909 and 26,000 in 1911, in which year Germany exported 1227 tons. In 1910 Russia produced more than 5000 tons of sodium bicarbonate and 6300 tons in 1912.

SODIUM PHOSPHATES

These are less soluble, and crystallise better than the potassium phosphates (*see* p. 416).

(*a*) **TRISODIUM PHOSPHATE :** Na_3PO_4 (Basic or Tertiary Phosphate). This is formed on saturating 1 mol. of phosphoric acid with 3 mols. of sodium hydroxide, better by evaporating a concentrated disodium phosphate solution (*see below*) previously neutralised with caustic soda (molecular proportions), or by fusing disodium phosphate (or the pyro- or meta-phosphate) with the calculated quantity of solid sodium carbonate or hydroxide. It crystallises from water in six-faced rhombohedral scales with $12H_2O$ (the decahydrate is also known), which are lost largely at 100°, although the last molecule is expelled only above 200°. The crystals with $12H_2O$ dissolve in five times their weight of water at 15°. With CO_2 the solution yields sodium carbonate and disodium phosphate.

---

[1] **Analysis of Soda.** The strength of pure soda solutions may be found from the Table of Specific Gravities (p. 591). In the case of soda ash it is necessary to heat it to gentle redness before analysis. The strength, or alkalinity, is determined with a normal solution of HCl, using methyl orange in the cold, or litmus with heating, as an indicator. The amount of insoluble matter is determined by dissolving 50 grams of soda in hot water and collecting the residue on a tared filter. The iron in this insoluble portion may be determined by the usual analytical methods. Sodium chloride is determined by titration with silver nitrate in a definite quantity of the solution which is first exactly neutralised whilst hot with nitric acid; a few drops of potassium chromate solution are used as indicator. The sulphates are precipitated with $BaCl_2$ in a solution of the soda which has been acidified with HCl, and heated, and the barium sulphate then weighed. Free sodium hydroxide, which may be present in certain qualities of the carbonate, is determined in 2 grams of the material by dissolving in water and then adding 10 c.c. of barium chloride solution (1 : 10); the whole is then diluted with hot water to 100 c.c., shaken, and allowed to settle in a closed bottle: 50 c.c. of the clear solution are withdrawn and titrated with a normal solution of HCl in presence of methyl orange, and the alkalinity thus found is calculated as NaOH and deducted from the total alkalinity first found in order to obtain the true content of sodium carbonate.

The aqueous solution has a strong alkaline reaction, since the anion PO_4''' is largely dissociated hydrolytically into PO_4H'' and OH' (*see* p. 271).

(*b*) **DISODIUM PHOSPHATE : Na_2HPO_4 (Neutral Phosphate, Secondary Phosphate, or Ordinary Sodium Phosphate).** This compound is ordinarily employed for chemical reactions because it is the most stable phosphate. It is obtained from dicalcium phosphate on precipitating the calcium with sodium carbonate :

$$PO_4HCa + CO_3Na_2 = CO_3Ca + PO_4HNa_2.$$

It is prepared on the large scale directly from bone ash or phosphorite by digesting it for several days with dilute H_2SO_4, by which means a solution of phosphoric acid and monocalcium phosphate is formed; this is then concentrated to separate the gypsum completely, filtered, diluted, and neutralised with Na_2CO_3, in order to separate all the remaining calcium. On concentrating the filtered solution the neutral phosphate crystallises out.

It crystallises from cold aqueous solutions with $12H_2O$ in large monoclinic prisms which melt at 35° and readily effloresce in the air; at 100° they lose $5H_2O$, and in a vacuum all their water; from solutions at a temperature higher than 30° it crystallises with $7H_2O$ and does not then effloresce in the air. One hundred parts of water dissolve 2·5 parts of Na_2HPO_4 at 0°, 5·8 at 15°, 9·3 at 20°, 15·4 at 25°, 39·3 at 35°, 82·5 at 50°, 91·6 at 60°, 95 at 70°, 96·6 at 80°, 97·8 at 90°, and 99·5 at 105°. The saturated solution boils at 106·4° and freezes at $-$ 0·45°. The heat of solution of the anhydrous salt is + 5·6 Cals., that of the heptahydrated salt $-$ 11 Cals., and that of the dodecahydrated salt $-$ 22·1 Cals.; dissolution of 14 parts of the latter in 100 parts of water at 11° lowers the temperature to about 4°. The aqueous solution is feebly alkaline, and when a little carbon dioxide is passed into it the reaction becomes amphoteric, that is, it reddens blue litmus paper and turns red litmus paper blue (as milk does, and also a number of organic compounds such as carbamide, amino-acids, dicyandiamide, urethane, nuclein salts, polypeptides, albumoses, xanthine bases, proteins, etc.) (*see* Vol. II., "Organic Chemistry").

It melts at about 300° after losing its water of crystallisation, and is then transformed into sodium pyrophosphate, $Na_4P_2O_7$, which crystallises with $10H_2O$, and is less soluble in water than disodium phosphate.

Crystallised commercial disodium phosphate costs £8 per ton, whilst the refined product costs £14 and the anhydrous product about four times as much. It is used in the preparation of enamels, in tinning and soldering (instead of borax), and as a weighting material in the dyeing of silk; it is also used in medicine. Italy produced 250 tons in 1905, 600 tons in 1907, of the value of £5640, 82 tons in 1914, and 56 tons in 1915.

(*c*) **MONOSODIUM PHOSPHATE : NaH_2PO_4 (Primary Phosphate or Acid Phosphate).** This product is obtained by boiling disodium phosphate solution with nitric acid and precipitating with alcohol, or by adding phosphoric acid to disodium phosphate solution until the latter gives no precipitate with $BaCl_2$. It crystallises with one molecule of water, which it loses at 100°, and is readily soluble in water, the aqueous solution having a weakly acid reaction. At 190° to 200° it is transformed into disodium pyrophosphate, $Na_2H_2P_2O_7$, and this at 220° forms tetrasodium pyrophosphate (*see above*), and at 240° sodium metaphosphate: $P_2O_7H_2Na_2 = H_2O + 2PO_3Na$; but other compounds are also formed, according to the conditions of heating, by condensation of one or more molecules of sodium metaphosphate, for example, $Na_2P_2O_6$, etc.

The molten metaphosphate dissolves metallic oxides forming orthophosphates: $PO_3Na + CuO = PO_4NaCu$. According to the nature of the metallic oxide variously coloured phosphates are so formed and are characteristic of the individual metals (*phosphate beads*, which are used in chemical analysis).

SODIUM HYPOPHOSPHITE, $NaH_2PO_2 + H_2O$ (*see* p. 414), is formed by decomposing a solution of calcium hypophosphite with sodium carbonate, filtering, and evaporating the solution in a vacuum, or by neutralising hypophosphorous acid solution with soda. It crystallises in square, deliquescent plates, soluble in absolute alcohol. In a vacuum it loses part of its water of crystallisation, the whole being expelled at 200°; at a higher temperature it yields the pyro- and meta-phosphates with liberation of H and PH_3. It undergoes oxidation to some extent in the air.

SODIUM PHOSPHITE, $Na_2HPO_3 + 5H_2O$ (*see* p. 415), is stable in the air and is obtained by neutralising phosphorous acid with sodium carbonate and concentrating *in vacuo*. The crystals effloresce over sulphuric acid and at 250° give PH_3 and sodium phosphate. With less soda, phosphorous acid gives *sodium acid phosphite*, $Na_2HPO_3, 2PO_3H_3 + H_2O$.

HYPOPHOSPHATES (*see* p. 417): The following are known: $NaH_3P_2O_6$ (monosodium), $Na_2H_2P_2O_6 + 6H_2O$ (disodium), $Na_3HP_2O_6 + 9H_2O$ (trisodium), $Na_4P_2O_6 + 10H_2O$ (tetrasodium), and $Na_5H_3(P_2O_6)_2 + 20H_2O$ (pentasodium dihypophosphate).

SODIUM BORATE. The most stable of the borates is **Sodium Tetraborate**, called **Borax**, $Na_2B_4O_7 + 10H_2O$, which has already been mentioned in connection with **Boric Acid**. It is found ready formed in certain lakes in India, China, Persia, and Thibet, from where it is sent to Europe under the name of *tinkal*. The minerals containing boron were mentioned on p. 506; common borax is known in monoclinic prismatic crystals, $Na_2B_4O_7 + 10H_2O$, and in octahedra containing only 5 mols. of water of crystallisation. The prismatic product is prepared by adding boric acid to a boiling solution of sodium carbonate (1 : 1) and allowing it to crystallise.[1] Much borax is now prepared from **Boronatrocalcite** (*Tiza*), $Na_2B_4O_7 + 2CaB_4O_7 + 18H_2O$, which is found in Chili, by boiling it with soda or by first preparing boric acid and then neutralising this with soda. Octahedral borax is obtained by cooling a solution of common borax of sp. gr. 1·26 (30° Bé.) to 70°, and collecting that portion of the crystals which separates at a temperature above 56°; the mother-liquors then yield ordinary borax. Its solubility in water is as follows: at 0° 2·83 per cent., at 20° 7·88 per cent., at 40° 17·90 per cent., at 60° 40·43 per cent., at 80° 76·19 per cent., and at 100° 201·4 per cent.

According to U.S. Pat. 911,695 (1909) by Bayley, borax is obtained much more economically by mixing borates in molecular proportions with sodium sulphate and heating to redness, but not to fusion, in suitable rotary furnaces similar to those used for Leblanc soda (p. 594); after cooling, the borax is dissolved in water and allowed to crystallise: $2Ca_2B_6O_{11}$ (colemanite) $+ 3Na_2SO_4 = 3CaSO_4 + CaO + 3Na_2B_4O_7$.

In 1906 and 1908 M. G. Levi proposed the preparation of borax by electrolysing tepid solutions of boric acid (cathodic) and sodium chloride (anodic) separated by a porous diaphragm; sodium borate is then formed at the cathode. The cathodes are formed of lead and the anodes of carbon; when the sodium chloride is replaced by sodium sulphate smaller yields are obtained. A good crystallisation of borax is obtained with a very small excess of soda. The process may be profitable where electric energy is cheap.

To obtain *anhydrous borax*, the hydrated salt is heated to dull redness in an iron pan, a glassy mass being obtained which is, however, always coloured, as it readily dissolves traces of metals. It may be obtained white without melting it (Ger. Pat. 241,893, 1911) by heating the powdered hydrate to 70° to 90° until the water content is reduced to 30 per cent. and then heating to 350° to 400°. Borax is used to facilitate the brazing of metals; these are joined in the hot in presence of borax by an alloy formed of 2 to 5 parts of copper and 1 part of zinc. Molten borax dissolves the metallic oxides and keeps the surfaces clean, preventing further oxidation, and the alloy thus comes into direct contact with the polished surfaces of the metals and brazes them firmly together. When brazing is unnecessary the metals are soldered with an alloy of tin and lead, in which case lower temperatures are used, and zinc chloride, ammonium chloride, colophony, or stearine are used as cleaning agents instead of borax. Borax is used for glazing earthenware, though borocalcite is now preferred. It is also

---

[1] Concentration of the solution yields, besides borax, also sodium metaborate and a salt of the composition, $NaBO_2 + 4HBO_3 + 3\frac{1}{2}H_2O$. If 4 equivalents of boric acid are mixed with 1 equivalent of borax at a certain concentration (10·5 litres of water, 10 kilos of boric acid, and 2·140 kilos of sodium carbonate, heated to complete solution of the boric acid), an acid *sodium borate*, $NaHB_4O_7 + 4\frac{1}{2}H_2O$, crystallises out. This salt crystallises unchanged from water in which it is highly soluble and yields solutions of syrupy consistency; it may hence be used advantageously as an antiseptic in place of borax. It does not redden phenolphthalein, and with silver nitrate it gives a white precipitate which turns brown in the hot (Ger. Pat. 244,778, 1909).

used in the manufacture of colouring matters, especially of anthracene dyestuffs. Further it is employed (ammonium borate best) as a means of rendering fabrics incombustible, and serves also as a mild antiseptic; considerable quantities are used with starch in the glazing and ironing of linen.

SODIUM PERBORATE (*sodium metaperborate*): $NaBO_3$, $4H_2O$, containing 10·39 per cent. of active oxygen. Since 1905 this salt has been used for the preparation of very pure hydrogen peroxide; its aqueous solution behaves like H_2O_2, evolves oxygen at 40°, and serves as an effective antiseptic in the treatment of sores. In 1898 Tanatar prepared it from hydrogen peroxide and borax or boric acid and caustic soda: $H_3BO_3 + NaOH + H_2O_2 = 3H_2O + NaBO_3$ or $Na_2B_4O_7 + 4H_2O_2 + 2NaOH = 5H_2O + 4NaBO_3$. To the boric acid suspended in a little water is added a small part of the caustic soda necessary for the reaction, the acid then passing into solution as polyborate. The calculated amount of hydrogen peroxide and the residue of the caustic soda are next added, the perborate beginning to crystallise out after a short time. The hydrogen peroxide was replaced later by sodium peroxide in order to obtain more concentrated solutions of the perborate; care must then be taken to neutralise immediately the caustic soda remaining free. Jaubert (Ger. Pats. 193,559 and 207,580) prepares the perborates by pouring a mixture of 12·5 kilos of boric acid and 16·3 kilos of sodium peroxide slowly into a very cold solution of 11 kilos of concentrated sulphuric acid in 170 litres of water, the temperature being prevented from exceeding 20°; the crystals separating are washed with alcohol and dried at 50°: $B(OH)_3 + Na_2O_2 = H_2O + NaOH + NaBO_3$. The solubility in water is about 2·5 per cent. at 15° and 3·8 per cent. at 32°; the solutions evolve a little oxygen at 40° and much above 60°.

Sodium perborate may be obtained (Ger. Pat. 237,608, 1910) by stirring with 5 per cent. hydrogen peroxide solution a mixture of the theoretical amounts of powdered sodium carbonate and borax until solution is complete; after an hour the perborate separates in crystals.

According to Ger. Pat. 218,569, the ready decomposition of the perborate during its formation and its contamination with sodium sulphate are prevented by replacing the sulphuric or hydrochloric acid by carbon dioxide, which does no harm even if present in excess. One hundred and fifty kilos of sodium peroxide are added to 200 kilos of water, avoiding any rise of temperature by the addition of ice. One hundred and fifty kilos of boric acid are then added and chimney gases freed from dust are passed through the liquid until 50 c.c. of the filtered solution decolorise only 5 to 10 c.c. of an $\frac{N}{5}$ solution of permanganate acidified with sulphuric acid.

When the reaction mass is neutralised with boric instead of sulphuric or hydrochloric acid, borax and polyborate are formed: $2Na_2O_2 + 8B(OH)_3 = 2NaBO_3 + Na_2B_6O_{10} + 12H_2O$; actually, however, a condensation product of these compounds, termed **perborax**, is obtained in crystals, $2Na_2B_4O_8$, $10H_2O$. This may be prepared also from borax and hydrogen peroxide: $Na_2B_4O_7 + H_2O_2 = H_2O + Na_2B_4O_8$. It is more soluble (about 7 per cent. at 22° and 14 per cent. at 32°) than the metaperborate and contains 4 per cent. of active oxygen and has a neutral reaction, whilst the metaperborate has an alkaline reaction and becomes more stable when heated *in vacuo* at 50°, after which only one molecule of water of crystallisation remains; after recrystallisation from a very little water, it then separates at once with $4H_2O$. Perborax is obtained solid directly as follows (Ger. Pat. 262,144, 1909): 100 parts of borax are mixed with 130 parts of finely pounded ice until the temperature is below 0°, 40 parts of powdered sodium peroxide being then added a little at a time; the mass liquefies without heating and is poured into shallow vessels, in which it sets to a crystalline mass. A. Poulenc (Fr. Pat. 411,258) attempted to obtain perborates by electrolysing an alkaline solution of boric acid (5 per cent.), but Pollak obtained negative results in this way. By electrolysing a solution containing 45 grams of borax and 120 of sodium carbonate per litre at 18° to 20°, K. Arndt obtained abundant formation of pure sodium perborate, possibly as a secondary product after the scission of the soda. A current density of 20 to 30 amps. per sq. dm. at 5 to 10 volts may be used. By repeated crystallisation from water and semi-neutralisation with acids, perborax is transformed into the ordinary perborate.

To render the perborate capable of storage, it must be obtained in large crystals (Ger. Pat. 204,279), and the prime materials must be pure and especially free from

Fe, Mn, etc., which act as negative catalysts (*see* pp. 71 and 583); either vessels with tinned cocks or wooden vessels are used.

In bleaching use is now made also of the perborates of magnesium, zinc, ammonium and potassium, KB_2O_5, $2H_2O$. Although costly in comparison with sodium peroxide (which has 20 per cent. of active oxygen in place of the 10·4 per cent. of the perborate) and with hydrogen peroxide, sodium perborate has the advantage of being usable in hot solutions in presence of soap, soda, sodium silicate, etc., of being stable up to 60°, and of corresponding with double its weight of hydrogen peroxide.

It costs from 2*s.* 5*d.* to 3*s.* 2*d.* per kilo (*see* p. 269). It keeps its strength well if crystallised, and is largely made to replace sodium peroxide and hydrogen peroxide as a detergent and bleaching agent, and to be used for oxygenated soaps, soluble starch, deodorants, decolorising agents, antiseptics, dentrifices, and oxygenated baths.

SODIUM SILICATE (Soluble Glass, Soluble Soda Glass, Water Glass). This compound was discovered in the Middle Ages by Van Helmont, but its preparation was precisely described by J. V. Fuchs in 1825. It was first employed, however, in the first half of the past century. It is similar to potassium silicate, and is obtained by melting 100 parts of powdered quartz with 56 parts of calcined soda; the soda may be replaced by a mixture of 70 parts of sodium sulphate with 4 parts of wood charcoal or sawdust. The molten mass is discharged from the furnace and after cooling is powdered and dissolved in 56 vols. of water with the aid of steam in autoclaves provided with stirrers, at high temperatures and under pressure. A heavy solution is thus obtained which is ready for sale. Whilst in the primitive furnaces with direct flame 1·5 kilos of coal were used for every kilo of silicate produced, to-day with the Siemens regenerative furnace (*see* Glass) the consumption of coal is only 0·29 kilo. The silicate obtained by fusion with alkali is the metasilicate, while that obtained from alkaline silicate with steam under pressure consists of the orthosilicate (*see* p. 502).

A double sodium and potassium silicate, more readily fusible than its components, is also used. In the furnaces the reaction occurs when the CO_2 is evolved from the soda or when the sulphate is transformed into sodium sulphite and then into Na_2O and SO_2, besides CO_2 and CO. If excess of coal is used, the mass is contaminated with Na_2S.

When the resulting molten sodium silicate has a brown colour due to the formation of Na_2S, this may be eliminated by passing a current of air through the molten mass or by adding copper oxide or lead oxide to the solution.

Soluble glass must be kept in closed vessels because the carbon dioxide of the air decomposes it with separation of gelatinous silicic acid.

In the solid state its composition varies between Na_2O, $4SiO_2$ and Na_2O, $2SiO_2$, and its solubility increases with diminution of the silica. Its greenish colour is due to impurities containing iron. Solid sodium silicate does not keep in the air so well as potassium silicate.

It dissolves slowly in cold water and the solution contains more alkali than the part which is still undissolved.

Soluble glass is used to render objects impregnated with it resistant to fire. It is used as an adhesive for glass, porcelain, stone, etc. It is much employed for adulterating (weighting) soap and in stereochromy as a medium for mineral pigments (zinc white and yellow, chrome green, etc.). It is also used in dyeing as a weak alkali.

Sodium silicate is placed on the market in solutions of 38° to 40° Bé. at a price of £2 16*s.* to £3 12*s.* per ton; of 50° to 55° Bé. at £3 4*s.* to £4 per ton, and the solid at £4 to £4 16*s.* per ton. A commercial silicate of 33° Bé. yielded on analysis 23·3 per cent. of SiO_2, 6·7 per cent. of Na_2O, 1·7 per cent. of chlorides and sulphates, and 67·6 per cent. of water. A sample of 40° Bé. contained 26·1 per cent. of SiO_2, 9·8 per cent. of Na_2O, 1·7 per cent. of impurities, and 62·4 per cent. of water.

Germany exported 4400 tons of the silicate in 1893, 11,600 tons in 1905, and more than 14,500 tons in 1913.

France exported 349 tons of sodium and potassium silicates in 1913, 315 tons in 1914, 171 tons in 1915, and 1194 tons in 1916.

The Argentine imported 23,900 tons in 1911. France imported 270 tons in 1913 and 83 in 1916. Austria exports about 100 tons per annum.

SODIUM AZIDE: NaN_3. This substance is obtained from organic compounds or preferably by heating sodamide in a current of nitrous oxide at 200°:

$$NH_2Na + N_2O = N_3Na + H_2O.$$

Its aqueous solution has a weakly alkaline reaction (*see* p. 376).

SODIUM CYANIDE: NaCN (*see* Potassium Cyanide, pp. 547 and 549). Mention may be made also of O. Liebknecht's patent (U.S. Pat. 969,885, 1910), according to which sodium cyanide is obtained by heating 7 kilos of metallic sodium to 700° in a covered cast-iron vessel and passing in 18 kilos of dry trimethylamine vapour: $N(CH_3)_3 + Na = NaCN + C + H + C_xH_y$ (hydrocarbons).

CHARACTERISTIC REACTIONS OF SODIUM SALTS. All sodium salts colour the Bunsen flame yellow and give a brilliant yellow line composed of two lines very close to each other in the spectrum. With potassium pyroantimonate, $Sb_2O_7H_2K_2$, the neutral salts of sodium give a white crystalline precipitate of acid sodium pyroantimonate, $Sb_2O_7H_2Na_2$, in the cold.

This reaction is one of the very few which permit sodium salts to be distinguished and separated from potassium salts.

LITHIUM: Li, 7

This is a somewhat rare element, but is widely diffused in small quantities. It is found in various mineral waters, for example, in those of Salsomaggiore, which are the richest known in lithium and strontium; also in the ashes of many plants, especially in those of beetroot, tobacco, and tea. It is also found in animal organisms. As silicate, combined with other metals, it forms certain minerals such as *lithiferous mica* (*lepidolite*), $K_4Li_4(AlF_2)_3Al_4(Si_3O_8)(SiO_4)_3$ (4 to 5 per cent. of Li_2O); as phosphate in *triphyllite* and *lithiophyllite*, $Li(FeMn)PO_4$ (8 to 9·5 per cent. of the oxide), and is also found more abundantly in *ambligonite*, $Li(AlF)PO_4$ (8 to 9 per cent. of oxide), and in *petalite*, $Si_4O_{10}Al(Li, Na, H)$, which occurs in Elba. Many of its minerals are found in North America.

It is a soft metal with a silvery lustre and was obtained by Bunsen and Matthiessen in 1855 by the electrolysis of lithium chloride or preferably of a mixture of LiCl and KCl. It melts at 180°, and has the specific gravity 0·59 (water = 1); it is thus the lightest metal known and floats even on petroleum, in which it is preserved in order to protect it from ready oxidation. It decomposes water more slowly than sodium; it burns at 200° with an intense white light differing from that of lithium salts, which colour the flame crimson red and give a characteristic brilliant red line in the spectrum together with a less brilliant orange line. Metallic lithium costs 3*s.* 2*d.* per gram, and when chemically pure 9*s.* 7*d.*

Lithium salts are similar to sodium salts and also have certain resemblances to those of magnesium. The carbonate is mostly used medicinally, for making lithia water, for fireworks, and particularly for Edison accumulators of a new type. The bromide is used for photographic purposes.

Lithium burns intensely in an atmosphere of hydrogen, forming **LITHIUM HYDRIDE, LiH**, which is a fairly stable white powder.

LITHIUM CHLORIDE, LiCl, crystallises in octahedra and deliquesces in the air.

Lithium may be separated from its soluble salts by means of sodium phosphate or sodium carbonate, as it forms a phosphate, Li_3PO_4 ($+ \frac{1}{2}H_2O$), and a carbonate, Li_2CO_3, which are almost insoluble in water; in this respect it resembles the metals of the second group.

Certain salts of lithium, especially the carbonate, and the salicylate to an even greater extent, and also mineral waters containing lithium, are used in medicine as a remedy for arthritis, renal calculi, stone in the bladder, etc. Pure lithium carbonate costs about 16*s.* per kilo. In the United States 1150 tons of lithium minerals, of the value of £4800, were treated in 1903, and 575 tons, of the value of £1000, in 1904.

AMMONIUM

When treating of ammonia we noted that in aqueous solution it may be considered to consist partially of a hydrate of ammonia, $NH_4^{\cdot} . OH'$, resulting from the combination of one of its molecules with one molecule of water, and that this substance must be supposed to be dissociated partially into two ions, the cation $NH_4^{\cdot}$ called *ammonium*, which behaves in all reactions as though it were an alkaline metal, and the anion OH', which is the cause of the alkaline reaction of aqueous ammonia. Dilute ammonia solutions conduct the electric current less than similar solutions of KOH, thus showing that a portion only of the ammonia is present as a hydrate; this is confirmed by the fact that the pressures of ammonia in solution follow Henry's law fairly closely, and thus the greater part of the NH_3 is not combined with H_2O. The monovalent ammonium ion forms numerous salts just as though it were a metallic element, and these salts have very great chemical and physical resemblances to potassium salts, with which they are ordinarily isomorphous. This ammonium group may even be separated by absorption by mercury, with which it forms an *amalgam* (a property characteristic of metallic elements only and not of their compounds). When, however, attempts are made to isolate this "*ammonium metal*" it is decomposed into NH_3 and H.

Ammonia in aqueous solution, being less dissociated than sodium and potassium hydroxides, forms an alkali or base which is much less energetic, and is therefore easily displaced from its salts by these other bases. Its basic action is diminished in presence of ammoniacal salts, because these increase the number of $NH_4^{\cdot}$ ions in solution, thus displacing the previous ratio between the ammonium $NH_4^{\cdot}$ and OH' ions, a ratio on which the basic power depends (p. 103).

Ammonium salts are solid, and are unstable towards heat.

AMMONIUM CHLORIDE : NH_4Cl (SAL AMMONIAC)

This compound was formerly obtained by burning camel's dung. It is prepared to-day, in the same way as ammonium sulphate, from the ammoniacal liquor of gas-works (*see* Ammonia, p. 356), and attempts have also been made to obtain it by decomposing ammonium sulphate with KCl. It forms a white crystalline substance of fibrous structure which sublimes without melting. It dissociates at 350° into two gases, NH_3 and HCl, which reunite again on cooling (*see* p. 41). This dissociation occurs only in presence of small traces of moisture which act catalytically, and since all catalysts which cause a certain reaction are also capable of producing the reverse reaction when external temperature conditions are suitably changed, in harmony with the law of mass and of chemical equilibrium, on mixing completely dry ammonia and hydrochloric acid no combination occurs; if water vapour is present, however, union immediately takes place at temperatures below that of dissociation.

Ammonium chloride is very soluble in water and the solution has a faint acid reaction because the $NH_4^{\cdot}$ ion hydrolyses with the minimal quantities of dissociated hydroxyl groups of the water, forming NH_3 and H_2O and leaving unaltered the $H^{\cdot}$ acid ions of the water. When heated, the solution loses part of the hydrolysed ammonia, and thus its acid reaction is increased because new quantities of ammonium cations, $NH_4^{\cdot}$, are hydrolysed, forming further free acid ions, $H^{\cdot}$.

Ammonium chloride is used in soldering because when heated it liberates HCl, which dissolves the oxides on the surface of the metals (*see* Borax, p. 605); it is used in dyestuff factories and in calico printing.

The crude commercial product costs about £26 per ton, and when purified £32. In 1902 Italy produced 120 tons, in 1914 65 tons, worth £2090, and in 1915 60 tons, of the value £2880. In 1911 England exported 7750 tons, of the value £186,960.

AMMONIUM CHLORATE: NH_4ClO_3. This is obtained by neutralising a solution of chloric acid with ammonia or ammonium carbonate or by precipitating calcium chlorate solution with ammonium carbonate, filtering and concentrating the filtrate, or by mixing ammonium tartrate solution with potassium chlorate, collecting the separated cream of tartar on a filter and concentrating the filtrate. It is very soluble in water and slightly in absolute alcohol, and the crystals melt and explode at 102°. In the light it turns yellow and may after a time explode.

AMMONIUM PERCHLORATE: NH_4ClO_4. This has assumed importance for the preparation of explosives (*see also* p. 540), e. g., *jonkite* (53·24 per cent. of the perchlorate + 32·30 per cent. of ammonium oxalate + 14·46 per cent. of trinitronaphthalene), *permonite*, and *persolite* (mixture of perchlorate, ammonium nitrate, and trinitrotoluene), etc.

It is obtained by heating sodium chlorate just to fusion, the resultant mixture of sodium chloride and perchlorate (*see* p. 193) being dissolved in a little hot water so as to leave undissolved almost all the NaCl; the solution is then concentrated and treated with concentrated boiling ammonium chloride solution. It forms large crystals stable in the air but decomposing into NH_4Cl and Cl when heated. It dissolves in five times its weight of water and is almost insoluble in alcohol. It costs about 1*s.* per kilo.

AMMONIUM FLUORIDE : NH_4F. This compound is obtained by the interaction of HF and NH_3, or by subliming a mixture of $NH_4Cl + NaF$. It forms deliquescent crystals which readily attack glass. On heating a solution of this salt a portion of the NH_3 is evolved and an *acid ammonium fluoride*, NH_4F, HF, remains, which is commonly used for etching glass. Pure ammonium fluoride costs £80 per ton; the doubly refined product costs £140 per ton and when chemically pure 6*s.* 5*d.* per kilo. The commercial crystalline acid fluoride costs £76 per ton and the chemically pure dry salt 3*s.* per kilo.

It is used as a disinfectant in the manufacture of spirits, beer, etc., and does not attack metallic objects very much. It is now more economically obtained in solution by utilising the silicon fluoride formed in superphosphate manufacture (*which see*).

AMMONIUM SULPHATE : $(NH_4)_2SO_4$

The preparation of this salt has been already described when dealing with ammonia (pp. 357 *et seq.*), and is based almost entirely on the distillation of coal for the manufacture of illuminating gas and metallurgical coke. The ammonia liberated from the ammoniacal liquor by heating with milk of lime is absorbed in sulphuric acid of 50° Bé., the sulphate being allowed to crystallise directly from the solution, which is heated by the reaction to 120°; excess of sulphuric acid is always maintained to decompose the thiocyanates and cyanides present, sulphuric acid free from nitrous acid being used so as to avoid brown coloration of the ammonium sulphate separating.

It forms a mass of white crystals isomorphous with potassium sulphate and it decomposes slightly even below 100°, and at 280° begins to sublime and decompose to a large extent in the same manner as all ammonium salts of polybasic acids, forming ammonia and *acid ammonium sulphate*, NH_4HSO_4. It is very soluble in water (in an equal weight at 100°), and the solution is slightly hydrolysed in the same manner as ammonium chloride solution. The process of Addie and Mond for absorbing ammonia in the distillation of coal, peat, etc., by washing the gas with sulphuric acid was improved according to Eng. Pat. 20,870 of 1904, U.S. Pat. 845,332, and Ger. Pat. 181,846 of 1909.

According to these patents the gas is cooled to the condensation point of the tar, the gas being then passed through a separator, reheated, and the ammonia absorbed by sulphuric acid. Each ton of coal distilled yields 8 to 12 kilos of ammonium sulphate, according to the quality of the coal and the type of furnace used. Collet and Eckardt (1910) proposed the preparation of ammonium sulphate by passing a stream of $SO_2 + NH_3 +$ air into water. The ammonium sulphite which is thus formed is transformed into ammonium sulphate by the action of the air; similarly by treating calcium cyanamide in the hot with SO_2 and steam soluble ammonium sulphite is obtained which is then oxidised, and insoluble calcium sulphite remains:

$$CaCN_2 + 2SO_2 + 4H_2O = CaSO_3 + CO_2 + SO_3(NH_4)_2.$$

By the Burkheiser process ammonium sulphate is obtained directly by means of the sulphur of the gas itself, no sulphuric acid being required. Feld prepares it by fixing ammonia and H_2S in a single apparatus.

USES. Most of the ammonium sulphate is used as a nitrogenous fertiliser (*see* pp. 348 and 577), for which purpose it should not contain thiocyanates, these being injurious to plants. It is also employed for making other ammonium salts and ammonia.

PRICES AND STATISTICS. The price varies somewhat, the agricultural product costing £11 to £14 per ton and the pure product £24. Owing to the great demand for ammonia for making ammonium nitrate and synthetic nitric acid (p. 398) for explosives during the European War, ammonium sulphate for agricultural purposes was sold at Genoa for £44 per ton in July 1917 and £64 per ton in February 1918.

Agriculture absorbs continually increasing quantities of the sulphate in comparison with sodium nitrate; thus, in Germany, whereas the consumption of sodium nitrate increased in twelve years by 65 per cent., that of ammonium sulphate increased in the same period by 300 per cent.

The ammonium sulphate made in France is obtained as to 30 per cent. from gas-works, 50 per cent. from coke furnaces, and 15 per cent. from sewage. In Germany 12 per cent. is obtained from gas, 85 per cent. from metallurgical coke, and 2 per cent. from sewage, and in England 60 per cent. from gas and 25 per cent. from coke furnaces. The world's output was 10,000 tons in 1860 and reached 1,450,000 tons in 1913 (*see* Table on next page).

Italy imports continually increasing quantities of ammonium sulphate for agricultural purposes: 5370 tons in 1903, 9738 in 1906, 16,700 in 1908, 20,750 in 1910, 21,190 in 1912, 13,110 in 1914, 7600 in 1915, and 2824 in 1916. In 1907 100 tons were produced from the boraciferous soffioni, and in 1914 5000 tons were made from ammonia derived from calcium cyanamide.

England exported 145,000 tons in 1900, 162,000 in 1903, 201,400 in 1906, 264,000 in 1909, 292,000 in 1911, and to the value of £4,400,000 in 1913. In 1908 the exportation was distributed thus: 24,000 tons to France, 24,500 to Germany, 9000 to Belgium, 51,600 to Spain and Portugal, 7300 to India, 7400 to Holland, 39,000 to Japan, 29,000 to the United States, etc. In the same year the output was obtained as follows: 168,000 tons from gas-works, 20,000 from blast-furnaces, 52,000 from distillation of shale and 85,000 (only 11,000 in 1898) from coke ovens and gas generators. The consumption in Great Britain is about 90,000 tons per annum.

In 1905 Germany imported 48,000 tons and exported 27,559 tons at £12 10*s*. per ton; in 1908 the imports and exports were 47,000 and 73,000 tons respectively, in 1909 58,000 and 58,000, in 1913 34,600 and 75,868 (£680,000); in the first half of 1914 74,723 tons were exported. In 1913 Germany produced 50,000 tons of ammonium sulphate from synthetic ammonia (p. 372).

Austria imported the sulphate to the value of £320,000 in 1913.

Japan imported 66,000 tons in 1908, 49,000 in 1909, 69,000 in 1910, 111,520 in 1913, 105,632 in 1914, 19,949 in 1915, and 7164 in 1916.

Before the war Belgium had an annual importation of about 20,000 tons of ammonium sulphate and an exportation of about 16,000 tons.

The United States imported 92,000 tons in 1910, 95,000 in 1911, 75,310 in 1914, 32,998 in 1915, and 13,170 in 1916.

PRODUCTION OF AMMONIUM SULPHATE IN DIFFERENT COUNTRIES (TONS)

Year	England (⅔ exported)	Germany	France	Belgium, Holland, Denmark and Scandinavia	Italy	Austria-Hungary	Spain	United States	Denmark	Belgium	Australia	Japan	Russia	Whole World
1896	193,865	55,000	45,600	35,000	1,523	—	—	—	—	—	—	—	—	365,000
1898	199,447	76,000	34,000	30,000	1,350	—	—	—	—	—	—	—	—	440,500
1900	216,195	130,000	37,000	35,000	2,147	—	—	—	—	—	—	—	—	493,000
1902	232,435	135,000	40,000	38,000	3,444	—	—	—	—	—	—	—	—	543,000
1904	249,182	175,000	43,000	39,000	3,837	—	—	—	—	—	—	—	—	557,500
1906	293,335	255,000	49,100	35,000	4,820	30,000	10,000	75,000	—	—	—	—	—	759,600
1908	318,710	300,000	57,600	50,000	5,350	35,000	20,000	82,000	—	30,000	—	2,500	—	850,000
1909	348,000	330,450	54,000	*Holland*	6,864	50,000	—	90,000	—	35,000	—	3,000	—	950,000
1910	369,000	375,000	56,000 (?)	5,000	7,172 (imports 21,000)	100,000	12,000	116,000 (imports 90,000)	—	36,000	—	4,000	—	1,100,000
1911	378,500	400,000	62,000	6,000	8,704	30,330	12,000	127,000	—	—	—	3,862	—	1,175,000
1912	394,000	492,000	69,000	6,000	11,100	35,500	12,000	149,700	2,400	43,700	3,000	7,300	4,000	1,300,000
1913	425,000	549,000	75,000	6,000	15,000	150,000	15,000	176,900	2,800	48,600	3,000	8,000	3,000	1,450,000
1914	431,000	—	—	5,000	14,323	—	16,000	166,000	—	—	3,741	16,035	17,176	—
1915	432,836	—	42,000	5,000	14,700	—	16,500	226,834	—	—	6,503	31,824	16,380	—
1916	445,029	—	25,000	4,000	—	—	18,000	294,835	—	—	7,214	38,203	32,760	—

France imported 25,000 tons in 1913, 9300 in 1914, 11,650 in 1915, and 25,200 in 1916.

On electrolysing ammonium sulphate, Ammonium persulphate $(NH_4)_2S_2O_8$, is obtained and is now employed commercially as an oxidising agent, because when its aqueous solution is heated it forms ammonium sulphate, sulphuric acid, and oxygen (*see* Persulphuric Acid, pp. 328 and 588). It is used for the preparation of other persulphates

AMMONIUM NITRATE : NO_3NH_4, forms very deliquescent white crystals, melts at 159°, has a bitter taste, and decomposes above 185° into $2H_2O$ and N_2O. This is not a simple dissociation, because on cooling this mixture the original product is not regenerated as in the case of ammonium chloride. The crystals produce cooling when they dissolve in water.

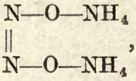
It is obtained by neutralising nitric acid with gaseous ammonia or ammonium carbonate and on evaporating the solution large crystals are formed. According to Ger. Pat. 178,620 and Norwegian Pat. 19,410 of 1908, it may be prepared by mixing a solution of calcium nitrate with excess of ammonia and passing carbon dioxide through the liquid:

$$Ca(NO_3)_2 + 2NH_4OH + CO_2 = CaCO_3 + 2NH_4NO_3 + H_2O.$$

It may also be obtained, according to Ger. Pats. 166,746 and 184,144, and Fr. Pat. 465,683 of 1913, from ammonium sulphate and sodium nitrate, either in solution or by fusion. It is best to use excess of the nitrate: 132 kilos of ammonium sulphate and 85 kilos of sodium nitrate are dissolved in 250 litres of water and the liquid concentrated at a temperature of 90°; after separation of the slightly soluble sodium-ammonium salt, water is added to form a saturated solution at 50°, the bulk of the ammonium nitrate then separating when the liquid is cooled to 20°. It may be obtained also from ammonium sulphate and calcium nitrate in an autoclave at 150°.

It serves to make explosives and safety explosives for mines and, when mixed with trinitrotoluene, for shattering explosives (*see* Vol. II., "Organic Chemistry"). Small amounts are used for freezing mixtures, and its future use as a concentrated nitrogenous fertiliser may be prophesied when it can be made cheaply by the partial oxidation of synthetic ammonia by the Ostwald system (*see* p. 398). At Notodden in Norway a factory was at work in 1912, producing 15 tons per day of very pure ammonium nitrate from synthetic ammonia made in electric furnaces. The price of the nitrate was about £40 per ton in 1912, but during the European War it rose to £160 per ton in Italy. The output of ammonium nitrate in Italy was 904 tons in 1915 and 14,700 in 1916, but in 1917 was increased largely, both in Rossi's electrochemical works at Legnano and in the new works of the Società Italiana Prodotti Esplodenti at Vado, which has a capacity of more than 2000 tons per annum.

AMMONIUM NITRITE : NH_4NO_2. This compound is formed by the action of an electric discharge on moist air. It forms a crystalline deliquescent mass which decomposes on heating or even in hot concentrated solution into $2H_2O + N_2$, with evolution of heat, so that it is not possible to recombine the products of the decomposition by pressure, the reaction being exothermic. In this case also the phenomenon is not one of dissociation, as is the case in the formation of sodium hydride.



AMMONIUM HYPONITRITE: $\begin{array}{l}N-O-NH_4\\ \| \\ N-O-NH_4\end{array}$, is obtained from gaseous NH_3 and an ethereal solution of hyponitrous acid: it melts at 64° with decomposition.

AMMONIUM CARBONATE : $CO_3(NH_4)_2$. This compound forms a transparent crystalline mass which sublimes at 60°, is rather unstable, and is obtained together with ammonia from **AMMONIUM BICARBONATE** (acid ammonium carbonate): CO_3HNH_4, which is the more stable and is formed from aqueous ammonia and CO_2. It is obtained pure from gaseous ammonia with CO_2 and steam, these being passed in molecular proportions into a hot tube discharging into a cooled chamber, in which it condenses as a white mass. It is, however, sufficient to pass CO_2 into water at 70° to 90°, so that the gas assumes the temperature of the water and also the necessary moisture, and then to pass it with NH_3 into the cooling chamber, where the carbonate condenses (Ger. Pat. 237,524 of 1909 and 246,017 of 1910). It is commonly prepared by sublimation from a mixture of equal parts of calcium carbonate and ammonium sulphate or chloride together with one-eighth of a part of powdered wood charcoal, the ammonium carbonate being then condensed. G. Castelfranco (1911) proposes to replace the calcium carbonate by magnesium carbonate (giobertite), so that the residue after sublimation consists of magnesium sulphate, which is of greater value than calcium sulphate. It is easily found ready formed in the commercial *sesquicarbonate,* which is a mixture of one part of ammonium carbonate with two parts of the bicarbonate and a little *ammonium carbamate,* $NH_2 . CO_2 . NH_4$. Horns of animals yield considerable quantities of ammonium carbonate when burned. The carbonate is highly soluble in water and in the air loses ammonia, water being absorbed and the bicarbonate formed at the surface.

It is used in making dyestuffs, for de-fatting fabrics, in medicine, for making pastry and in baking in place of yeast to cause the dough to rise; it is also mixed with other salts for extinguishing fires.

The production of ammonium carbonate in Italy was 55 tons in 1914 and 75 tons in 1915, most being used in baking pastry; prior to 1910 the importation amounted to about 350 tons. England exported 3300 tons in 1909 and 3800 in 1910.

It costs £36 per ton and is made principally in England; Germany imported 673 tons in 1908.

The *sesquicarbonate* is obtained by heating a mixture of ammonium sulphate or chloride with calcium carbonate.

AMMONIUM PHOSPHATES. Normal triammonium phosphate is not known because it is not stable, although phosphoric acid is tribasic; mono- and di-ammonium phosphates of little importance are, however, known.

SODIUM AMMONIUM PHOSPHATE (Secondary Phosphate) : PO_4NaHNH_4 (Phosphorus Salt or Microcosmic Salt). This is the most important of the various ammonium phosphates and is found in guano and in fermented urine. It is obtained by crystallising a mixture of disodium phosphate and ammonium chloride:

$$Na_2HPO_4 + NH_4Cl = NaHNH_4PO_4 + NaCl.$$

When melted, it loses water and ammonia, forming a vitreous mass of sodium metaphosphate, $NaPO_3$, which when fused dissolves various metallic oxides forming metallic orthophosphates of various colours according to the nature of the metal (*phosphate bead*).

AMMONIUM SULPHIDE : $(NH_4)_2S$. This compound is obtained from H_2S and NH_3 at − 18°, but at ordinary temperatures even in aqueous solution it decomposes to form $NH_3 + NH_4SH$ (*ammonium hydrosulphide*). At 45° it dissociates into 2 vols. of NH_3 and 1 vol. of H_2S. On passing hydrogen sulphide into a concentrated solution of ammonia until this is completely saturated,[1] a solution of ammonium hydrosulphide, NH_4SH, is obtained, and if the same volume of ammonia as was first employed is added to this, a solution of normal ammonium sulphide, $(NH_4)_2S$, is obtained.

AMMONIUM HYDROSULPHIDE : $(NH_4)SH$. This compound is obtained in a crystalline condition by passing a current of H_2S into an alcoholic solution of ammonia. The aqueous solution obtained as described above becomes yellow on standing in the air, because the hydrogen sulphide which is formed by hydrolysis oxidises in the air with separation of sulphur, and this dissolves in the ammonium hydrosulphide, forming *ammonium polysulphides,* $(NH_4)_2S_x$, which are also obtained directly by heating ammonium hydrosulphide with sulphur. The pure solid hydrosulphide dissociates at 45° into 1 vol. of NH_3 + 1 vol. of H_2S.

The solution of the hydrosulphide is used in the laboratory in analysis for the precipitation of metallic sulphides which cannot be separated otherwise owing to their solubility in acids. The yellow hydrosulphide is used for dissolving those metallic sulphides capable of forming thio-acids which form soluble ammonium salts. Ammonium sulphide is used in organic chemistry as a reducing agent.

GENERAL REACTIONS OF AMMONIUM SALTS. They are all volatile and decompose on heating; the other bases (alkalis or alkali earths) drive off ammonia from solutions of ammonium salts on heating.

Chloroplatinic acid gives a yellow crystalline precipitate of *ammonium platinichloride,* $(NH_4)_2PtCl_6$, only slightly soluble in water, with ammonium

---

[1] In order to determine easily whether a liquid is saturated with a gas 8 to 10 c.c. are placed in a test-tube and the liquid is then shaken strongly after closing the mouth of the test-tube with the thumb. If pressure is produced in the tube, as is easily observed on lifting the thumb, it is a sign that the liquid was saturated, but if suction is produced, this was not the case.

salts. Excess of tartaric acid also forms a slightly soluble acid ammonium tartrate.

SECOND GROUP OF THE METALS

These are all *divalent*, and are divided into three sub-groups, in accordance with certain analogies in their chemical and physical properties:

(*a*) **Calcium, Strontium, Barium**; (*b*) **Glucinum, Magnesium**; (*c*) **Zinc, Cadmium, and Mercury.**

ALKALINE EARTH METALS

Ca, 40.09 ; Sr, 87.6 ; Ba, 137.37

These metals are thus called because, on the one hand, their oxides are similar to those of the alkali metals, and present, on the other hand, certain similarities to the earths (alumina, etc.).

With increase of the atomic weight and atomic volume their basicity increases; thus the derivatives of barium are more stable than those of calcium, which is also in harmony with their heats of formation. They combine directly with nitrogen, forming nitrides, in common with lithium and magnesium.

They are easily distinguished from the alkali metals because they form insoluble carbonates, sulphates, and phosphates. They have no great affinity for oxygen, although they cannot be obtained in the free state by reducing their oxides with carbon because these oxides melt only at extremely high temperatures in the electric furnace, and at such temperatures the alkaline earth metals which are liberated immediately react with carbon to form carbides.

CALCIUM: Ca, 40.09

This element is very abundant and widely diffused in nature, especially as calcium carbonate in the form of *marble, chalk, calcspar*, etc.; as phosphate in *phosphorite;* as sulphate in *gypsum, anhydrite*, and *alabaster;* as fluoride in *fluorspar;* as a pure silicate, $CaSiO_3$, in *wollastonite*, etc. It also abounds as a component of various other rocks, and is found in all vegetable and animal organisms, in egg-shells, sea-shells, etc.

Calcium was discovered by Davy in 1808, and was prepared in the pure state by Bunsen in 1855. Moissan obtained it later by heating calcium iodide to a dark red heat with an excess of sodium, which also served to dissolve the metallic calcium as it was formed; after cooling, the sodium was separated by dissolution in absolute alcohol, and calcium thus remained in the form of a lustrous crystalline powder. Metallic calcium is now obtained by the process of Ruff and Plato (Ger. Pat. 153,731) by electrolysing at 800° a mixture of 100 parts of $CaCl_2$ and 16 parts of CaF_2, melting at 660°; graphite is used as the anode and an iron wire as the cathode, pure calcium of 99·3 per cent. being deposited on the latter. Other electrolytic processes are given in Ger. Pats. 144,667 and 155,453.

In dry air metallic calcium keeps fairly well, but in moist air it becomes covered with a layer of hydroxide. Calcium decomposes water in the cold with considerable evolution of energy. It has a silvery lustre, which is slightly yellowish in shade. Its specific gravity is 1·83, and it is harder than tin. It has a great absorbent power for gases and can be used for the production of a vacuum in various media. It melts at a red heat (780°) and burns with an orange-red flame. Its vapours combine readily with oxygen and nitrogen. One gram of calcium formerly cost 17*s*. 6*d*.; it is now prepared industrially at

9*s*. 7*d*. to 12*s*. per kilo, and is employed in metallurgy for removing the last traces of carbon from alloys and metals by melting them with a little calcium. It serves as a good reducing agent in organic chemistry and is used instead of magnesium in Grignard's reaction. Certain metallic alloys containing calcium are of special interest.

CALCIUM NITRIDE : Ca_3N_2. This is a brown substance obtained by heating calcium to a red heat in a current of nitrogen; it is decomposed by water, forming calcium hydroxide and ammonia.

CALCIUM HYDRIDE : CaH_2. This compound is formed in the cold, but the reaction proceeds more rapidly on heating by the direct interaction of Ca and H_2. It is a grey powder which decomposes water energetically with evolution of hydrogen, and it has therefore been proposed for filling balloons.

CALCIUM OXIDE : CaO (QUICKLIME)

The practical importance of this substance is universally known. The chemically pure product is obtained in the laboratory by heating pure calcium nitrate or carbonate to redness. Industrially limestone is used; this occurs in large deposits and is often found as pebbles in river beds. On heating this limestone in intermittent or continuous kilns to about 1000° all the CO_2 of the carbonate escapes and CaO remains.

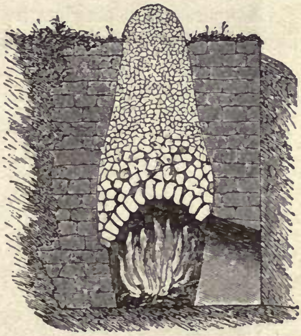


FIG. 241.

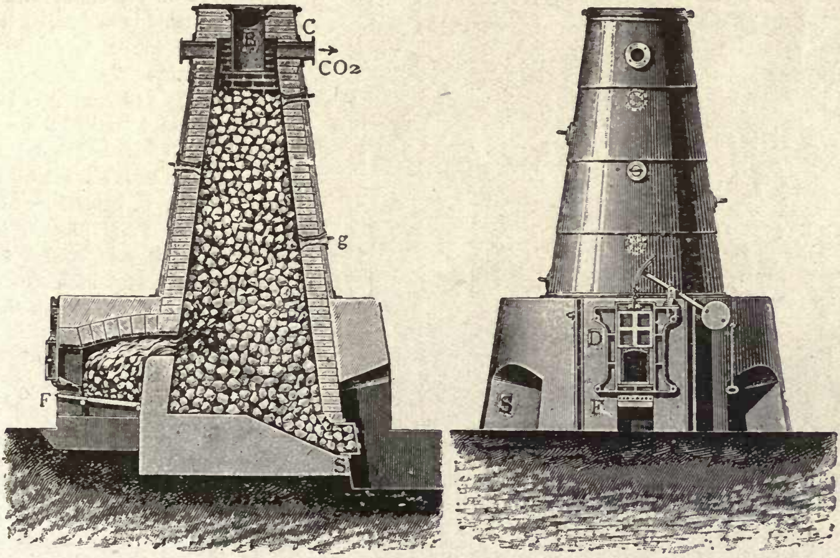


FIG. 242.

In order to dissociate 1 kilo of $CaCO_3$, 425 Cals. are required, and since 1 kilo of coal produces 8000 Cals., $\frac{100 \times 425}{8000}$, *i. e.*, 5·3 kilos of coal will be theoretically required in order to decompose 100 kilos of calcium carbonate into $CaO + CO_2$. In practice, however, the best lime-kilns (those of Hoffmann, Dietzsch, etc.) use about 10 to 12 kilos of coal.

The type of kiln mostly used in the past was distinguished by its simple construction; it consisted of an open channel formed of brickwork and was filled from above (Fig. 241).

Large pieces of limestone were first arranged to form an arch (temporarily supported by wood) on which smaller pieces were placed. The fuel was burnt at the lower part of the furnace, but the heat was not well utilised, and 500 to 600 kilos of wood were used per cu. metre of lime, which weighed 1400 to 1600 kilos; each operation, producing 10 to 20 cu. metres of lime, takes from 40 to 45 hours. It is finished when the limestone blocks have become white hot, and have somewhat decreased in volume (about one-sixth). The kiln is then allowed to cool for twelve hours, is discharged at the lower part which has served as a hearth, and is again charged.

A furnace for continuous work in which the heat is better utilised and the carbon dioxide recovered is illustrated in section and perspective in Fig. 242, in which the heating is produced by three lateral hearths with grates, *F*, these alternating with three discharging openings, *S*. The limestone is charged in above from cars by means of inclined planes or elevators, through the mouth, *B*, which is immediately closed so that the carbon dioxide may be collected in the upper tubes, *C*; the progress of the burning of the lime is watched by observing the red-hot limestone through the windows, *g*, and the temperature and the draught are regulated by means of the damper, *D*.

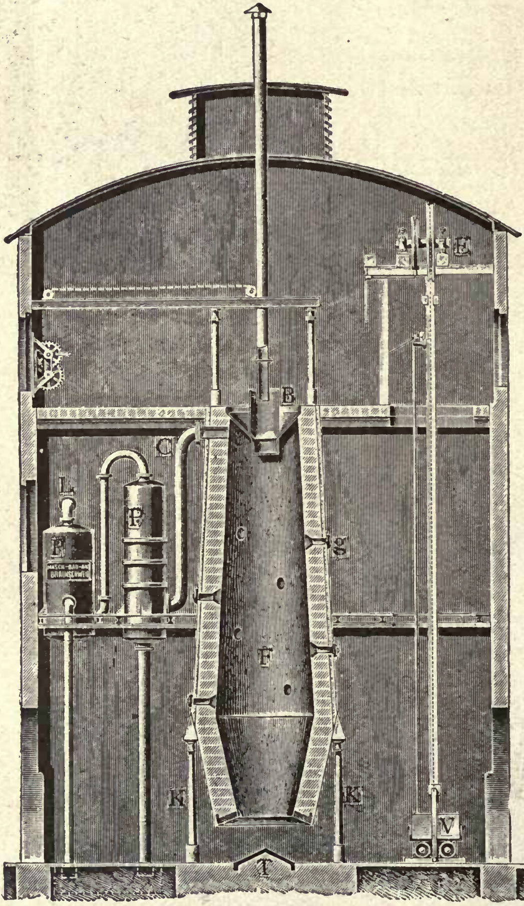


Fig. 243.

Another form of continuous kiln, much used in sugar factories, where both the lime and the carbon dioxide are utilised, is shown in Fig. 243. In this there are no lateral hearths, but it is charged from above with a mixture of limestone and coke which is raised in cars, *V*, by the elevator, *E*; the kiln, *F*, is formed of a sheet-iron shell of conical form constricted below and lined internally with a layer of firebrick. The whole of the furnace is raised above the ground, and supported by cast-iron columns, *K*. The whole weight of the limestone and coal with which it is charged is supported by the conically raised floor, *T*; the interval which separates the lower mouth of the kiln from the floor allows the quicklime to be removed gradually and allows sufficient air for the combustion to enter. The small side-windows, *g*, permit the progress of the burning to be observed. The carbon dioxide which collects above is led by the tube *C* to a washing apparatus, *P*, and then passes through the tube *L* into the exhaust pump.

In certain cases the circular Hoffmann furnace which is generally adopted in the ceramic industry is used (*see* Porcelain), and economises fuel very considerably. There are also somewhat complex gas-fired kilns which we shall not describe here; it is said that in America rotary furnaces have been employed, similar to those used for cement, which require about 8·5 kilos of coal per 100 kilos of limestone.

The proportions of limestone, coal, and air in the lime-kilns of the Solvay Soda Works are adjusted in such a manner that the gas collected above contains about 32 per cent.

of CO_2 (never less than 28 per cent.), the charges being introduced only every three hours and not more frequently. When the CO_2 is to be utilised coke is used instead of coal in order to obtain the gas in a purer state.

Commercial quicklime always contains a little silica, alumina, and iron oxide, which sometimes give it a slightly yellow or grey colour.

The limestone used for the production of quicklime should not contain much magnesia, because 6 to 8 per cent. of this ingredient is sufficient to cause the formation of poor lime (of poor quality), and when 20 per cent. is present the lime is useless; those quicklimes which contain little magnesia are called *fat* (or *rich*) limes.[1]

When pure, calcium oxide forms a whitish mass which melts only at about 2572° and then volatilises. When heated in the oxy-hydrogen flame it emits an intense white light (Limelight, p. 190).

Calcium oxide absorbs water very actively, combining with it with evolution of much heat (1 kilo of CaO gives 280 Cals.) and transformation into a voluminous amorphous mass of **calcium hydroxide, $Ca(OH)_2$ (slaked lime).** On standing in the air it absorbs CO_2 and H_2O vigorously and may thus be used as a dehydrating or drying agent.

Quicklime is used for the preparation of slaked lime and therefore of mortar, and also for the manufacture of crucibles which resist high temperatures (for melting platinum in the oxy-hydrogen flame); it is also used in glass manufacture and in the smelting of metals. Italy produced 28,000 tons, of the value of £11,200, in 1907 for this latter purpose, and in 1911 imported 794 tons. England produced 4,436,923 tons of lime in 1909 and 4,631,432 in 1910. For masonry constructions alone the United States consumed in 1911 3,500,000 tons, of the value of about £2,800,000.

CALCIUM HYDROXIDE : $Ca(OH)_2$ (SLAKED LIME)

When quicklime is moistened with about one-third of its weight of water heat is developed [$CaO + H_2O = Ca(OH)_2 + 15{\cdot}5$ Cals.], and the temperature rises to 160°. There results a white powdery swollen mass of slaked lime, which when mixed with a further three or four parts of water forms a soft homogeneous paste which is kept in a trench dug out of the ground, where it loses the excess of water together with soluble alkali salts which would spoil the mortar owing to the production of efflorescence in the brickwork.

Calcium hydroxide is a white mass, only slightly soluble in cold and less in hot water, so that the cold solution (lime water) becomes turbid when heated. One part of lime dissolves in 760 parts of water at 0°, in 776 parts at 15°, in 813 parts at 20°, in 885 parts at 30°, in 962 parts at 40°, in 1044 parts at 50°, in 1158 parts at 60°, in 1330 parts at 70°, and in 1482 parts at 80°. The aqueous solution has a strongly alkaline reaction because the hydroxide is partly dissociated into $Ca^{\cdot\cdot}$ and $2OH'$. Slaked lime does not lose all its water even at 300°, and only regenerates the oxide at a red heat. It absorbs CO_2 from the air, being slowly transformed into carbonate.

The solubility of calcium hydroxide in water does not vary much with the temperature, and a saturated clear solution at the ordinary temperature contains 1·3 grams of $Ca(OH)_2$ per litre.

USES OF LIME. Lime is used in the preparation of sodium and potassium hydroxides from the carbonates. It is also used in the manufacture of chloride

---

[1] In Lombardy, however, lime obtained from dolomitic limestone is often used, this containing magnesia; although when magnesia is present in small quantities it weakens the lime and is an inert component, if present in large quantity it gives equally good lime; thus, the following limestone: $CaCO_3 = 54{\cdot}8$ per cent., $MgCO_3 = 44{\cdot}8$ per cent., $SiO_2 = 0{\cdot}1$ per cent., iron oxide and alumina $= 0{\cdot}2$ per cent., gives a fat strong (*i. e.*, weakly hydraulic) lime.

of lime by absorbing chlorine and in the recovery of ammonia from gas liquor, and largely in sugar refineries, candle works, etc.

The largest quantity is, however, used for the preparation of common mortar for building purposes by mixing it with water and sand; this mortar hardens slowly in the air (not under water) because a large portion of the lime absorbs CO_2 from the atmosphere and is thus transformed into carbonate, which then becomes crystalline and very hard.

For each cu. metre of fat slaked lime 3 to 5 cu. metres of sand are required, whilst with weak lime not more than 2 cu. metres can be used.

In 1903 Italy produced 830,850 tons of fat lime, of the value of £510,640, 842,000 tons in 1906, and 858,000 tons in 1908.

CALCIUM PEROXIDE : CaO_2. When hydrogen peroxide is mixed with lime water, calcium peroxide separates in crystals containing $8H_2O$. It loses water at 130° and parts with its oxygen at a red heat. It is to-day prepared from sodium peroxide and a calcium salt. Attempts were made to use it for bleaching textile fibres, but its cost is too high (£2 per kilo).

SODA-LIME. This product is obtained by heating a mixture of equal parts of powdered sodium hydroxide and calcium hydroxide to redness. It is obtained pure and of homogeneous composition in small quantities by quenching, for example, 80 grams of pure powdered calcium oxide (from marble) with a hot solution of 20 grams of NaOH in 60 grams of water in a porcelain crucible. The mixture is immediately and rapidly stirred and then heated directly over a flame in order to drive off all the water. When it is cooled the mass detaches itself from the crucible and is crushed in a mortar, the granulated soda-lime so obtained being kept in well-closed glass vessels. It is used as a drying agent and for absorbing CO_2; it absorbs also hydrogen sulphide, mercaptans, mustard oils, ethers, and hydrocyanic acid. It costs 7*d.* per kilo.

CALCIUM CARBONATE : $CaCO_3$

Calcium carbonate is found abundantly in nature in the form of *limestone* as the principal component of entire mountain chains, forming compact masses of very fine grain, generally amorphous, mixed with clay and with other minerals. When pure, however, and of granular crystalline structure it forms large deposits as *marble*. Dolomitic mountains are composed of a mixture of magnesium and calcium carbonates in which the latter preponderates.

The important deposits of true *chalk* consist of pure amorphous carbonate formed of microscopic remains of small marine animals. Many stalactites also are formed of calcium carbonate.

Calcium carbonate is widely diffused throughout the vegetable and animal kingdoms; egg-shells, corals, and pearls contain large quantities of calcium carbonate, as do also the bones of vertebrate animals.

It crystallises in two systems, that is, it is dimorphous and thus forms *aragonite* in rhombic prisms of sp. gr. 3, and *calcite* in hexagonal rhombohedra of sp. gr. 2·7, and when the latter is sufficiently pure and transparent it goes by the name of *Iceland spar*, which is used in optical instruments; it is isomorphous with $MgCO_3$, $ZnCO_3$, $FeCO_3$, and $MnCO_3$, whilst aragonite is isomorphous with $BaCO_3$, $SrCO_3$, and $PbCO_3$. According to W. Meigen (1910) aragonite is distinguished from calcspar by the fact that the former, when powdered, colours a hot cobalt nitrate solution violet, whilst the latter colours it blue; also ferrous sulphate solution yields a dark green and a yellow precipitate with aragonite and calcspar respectively. When calcium carbonate is precipitated from dilute solutions in the cold, crystals of calcspar are formed, but in the hot aragonite; from concentrated solutions it is precipitated in the amorphous state, but on heating crystals are formed which appear to be aragonite, whereas their behaviour with manganese sulphate solution shows that they consist of another form of calcium carbonate, namely, *vaterite*. These reactions show that, besides different crystalline forms, the different varieties of calcium carbonate possess different molecular magnitudes.

When heated to redness calcium carbonate loses 44 per cent. of CO_2, and calcium oxide, CaO, remains in the form of a white porous mass. The evolution of CO_2 is more rapid and complete if the gas is carried away by a current of air or steam as fast as it is formed. The temperature of decomposition of the carbonate varies with the pressure, and thus at 56 mm. pressure dissociation occurs at 625°; at 255 mm. at 740°; at 678 mm. at 810°; at 763 mm. (the ordinary pressure) at 812°, and at 1333 mm. at 865°. Practically, however, at ordinary pressure and with rapid heating dissociation does not occur at 812°, but only towards 925°, although even at ordinary pressures it may fall to 800° if the heating of the carbonate is not rapid and the CO_2 is immediately removed as fast as it is formed by a current of air or preferably of superheated steam. This fact is explained by remembering that the temperatures indicated above at which the dissociation of the carbonate occurs depend also on the *partial pressure* due to the CO_2 evolved; we have thus a behaviour analogous to that explained on p. 320, in connection with the catalytic formation of sulphur trioxide.

When CaO is heated in a vessel containing CO_2, recombination occurs in the proportions indicated by the dissociation pressures. On the other hand, when calcium carbonate is heated in closed vessels at a high temperature (about 1289°) no dissociation occurs, because at these temperatures the pressure is so great (110 atmos.) that the carbonate melts, and when it resolidifies assumes a crystalline granular form similar to that of Carrara marble (*artificial marble*); this was shown first by J. Hall in 1805 and afterwards by Rose and Siemens in 1863.

Calcium carbonate is almost insoluble in pure water, and its extremely small solubility may be determined (in common with that of other very slightly soluble substances) by a determination of the electrical conductivity of the solution. The carbonate is more soluble in water containing CO_2, because the primary carbonate or calcium bicarbonate, $Ca(CO_3H)_2$, is then formed, which is soluble in water in the proportion of 0·385 gram per 1000 grams of water. This fact explains why all natural waters contain more or less calcium bicarbonate, which readily loses CO_2 again, and thus becomes insoluble; one is thus able to understand also how the so-called scale is formed in boilers, how stalactites are formed, etc.

Calcium carbonate is decomposed by acids with evolution of all the CO_2 it contains.

If a soluble carbonate such as Na_2CO_3 is added to a soluble calcium salt, insoluble calcium carbonate separates; the precipitate is at first amorphous, but rapidly becomes crystalline. In the hot these crystals take the form of aragonite which is slowly transformed into crystals of calcspar. Aragonite is less stable than calcspar, and that which is now found in nature is undergoing slow transformation into calcspar; this change occupies thousands of years, although at 300° the transformation occurs very quickly.

When limestone has a very fine compact grain and shows parallel stratification, it is used for the preparation of *lithographic stones*, which have a yellowish homogeneous appearance, are of hardness 3 on the Mohs scale, and can be perfectly polished by suitable machinery, in which condition they are able to receive the finest imprints.

The lithographic stones of Pappenheim and of Solenhofen in Germany are world-famed. For some years good lithographic stones have been obtained from Sardinia (Bannei) and Cagli (Pesaro); the latter quarry yielded 200 tons of stone in 1908.

In England 11,811,122 tons of limestone were produced in 1909 and 12,512,736 tons in 1910.

Calcium carbonate in the form of *marble* is of great industrial importance and abounds in Italy, the most valuable coming from the Apuan Alps. Commercially two forms of marble are distinguished, namely, that of compact structure called *oriental alabaster*, and that with a crystalline or saccharoid structure (*statuary marble*), that of Carrara being renowned for its whiteness and clearness. There are also the most varied coloured marbles of varying value. One cu. metre of marble weighs about 2 tons. In 1905 a single block of 15,000 cu. metres of red statuary marble was obtained from the Baveno quarries in Lombardy.

The Italian production and exportation of the various qualities of marble are as follows:

Year	Output in tons		Exports in tons	
	Total	Apuan Alps	Crude Marble	Alabaster Marble as statuary, etc.
1890 . . .	275,829	240,600	—	—
1900 . . .	310,336	275,929	70,000 ?	80,000 ?
1905 . . .	389,869	342,132	132,765	95,229
1906 . . .	430,202	382,395	148,579	100,718
1908 . . .	425,600	369,900	155,398	103,867
1910 . . .	460,000	400,000	169,441	124,570
1912 . . .	522,088	447,584	200,000	160,949
		(£893,120)	(£680,000)	(£920,000)
1913 . . .	509,342	426,677	182,874	152,746
1914 . . .	431,087	357,227	151,894	108,639
1915 . . .	246,883	157,493	48,219	108,000
1916 . . .	—	—	49,919	82,000
1917 . . .	—	—	35,591	48,000

The difference between the total output and that of the Apuan Alps is obtained from Venetia (two-thirds) and Lombardy (one-third).

Of the 447,584 tons of the raw product produced in the Carrara district, 212,000 tons were sawn up, yielding 171,800 tons of commercial product of the value £770,400, whilst 44,500 tons were worked up in various ways without sawing and gave 17,800 tons of commercial products worth £272,000.

Italy also produces about 3000 tons of powdered marble, which is sold at 4*s.* per ton. In normal times the mining district of Carrara alone employs more than 12,000 workpeople.

The price of white Carrara marble at the quarry is 4*s.* 10*d.* to 5*s.* 7*d.* per sq. metre 2 cm. thick, 5*s.* 7*d.* to 8*s.* for that 3 cm. thick, 8*s.* 10*d.* to 12*s.* 10*d.* for 5 cm. thick, and 10*s.* 5*d.* to 14*s.* 5*d.* for 6 cm. thick; the price for blocks is £8 to £10 per cu. metre. Cipollino (Greece) marble costs £28 to £32 per cu. metre. Rough marble is sold at about £1 16*s.* per ton.

CALCIUM CHLORIDE : $CaCl_2$

This salt occurs in nature combined with magnesium chloride as *tachhydrite*, $2MgCl_2, CaCl_2, 12H_2O$.

It is obtained as a by-product in various industrial processes, such as the manufacture of ammonia soda, and is obtained pure by dissolving pure marble in HCl and evaporating to dryness; it then forms a porous mass.

It is very soluble in water (100 parts of water dissolve 37 parts of $CaCl_2$ at 0°; about 41 parts at 14°; 45·5 parts at 25°; and 50·67 parts of $CaCl_2$, or 99·97 parts of crystallised $CaCl_2, 6H_2O$ at 29·5°). On dissolving the crystalline product a strong cooling effect is produced, whilst on dissolving the anhydrous product the reverse is the case;[1] by mixing with snow the temperature may be lowered to — 48°. This substance crystallises with $6H_2O$ in transparent hexagonal prisms which are deliquescent in the air, melt at 29°, and then readily lose 4 mols. of water, whilst the last 2 mols. are removed only above 200°, leaving a white, porous, very hygroscopic mass which melts only at 806°. On then melting the $CaCl_2$ and allowing it to solidify, a compact crystalline mass is obtained, which readily absorbs water and is employed as a good dehydrating agent for drying gases and removing water or moisture from other liquids, such as ether, etc. It is most efficacious for drying gases when in a spongy condition, and if not too costly may be used industrially (for drying blast furnace gases); to dry air with $CaCl_2$ costs 25 per cent. less than when

---

[1] When a gram-molecule of $CaCl_2$ is dissolved in 6 mols. of water, 6·66 Cals. are generated; in 7 mols. of water, 5·57 Cals.; in $8H_2O$, 4·45 Cals.; in $9H_2O$, 3·71 Cals.; in $10H_2O$, 3·08 Cals.; in 15 H_2O, 1·77 Cals. and in $50H_2O$, 0·92 Cal. When a litre of solution $CaCl_2, 6H_2O$ is diluted

ice machines are used, and it may be economically regenerated if employed until it has absorbed only one molecule of water ($CaCl_2 + H_2O$), since it then remains solid and at 240° loses all its water again. In 1911 the Differdingen Iron-works had in use a plant capable of drying 30,000 cu. metres of air per hour, the moisture being reduced from 8 to 1·5 grms. per cu. metre by means of three towers containing altogether 72,000 kilos of $CaCl_2$ in layers 25 cm. thick. After eight hours the chloride is heated by the flue gases, being brought up to 240° in four hours, then allowed to cool for three hours and again used for drying.

It cannot be used for drying gaseous NH_3 because it combines with this gas forming $CaCl_2, 8NH_3$. The crude product is also used in 5 to 10 per cent. solutions for watering roads as its use prevents the formation of dust, but it leaves a viscous dust which sticks to the wheels of vehicles and to the shoes of pedestrians. It is used in dressing textiles, like magnesium chloride (*q.v.*).

When the anhydrous chloride is melted at a high temperature in presence of moist air, it partly decomposes into CaO and HCl.

Attempts to prepare chlorine and hydrochloric acid from calcium chloride (*see* pp. 156 and 178) have not given profitable results, and even if it were first converted into magnesium chloride—which decomposes more easily—there is such an abundance of this in the mother-liquors of the Stassfurt salts and elsewhere that it would not pay to prepare it.

The crude fused product obtained in Solvay soda-works (p. 598) is generally used in artificial ice factories for the cooling brine (30 to 35 per cent. of $CaCl_2$), as the solution does not freeze even at 18° to 19° below zero (*see* p. 261).[1] This crude chloride contains 70 to

---

with 250 c.c. of water, 13·5 Cals. are evolved; with 500 c.c., 19·5 Cals.; with 750 c.c., 22·2 Cals.; with 1 litre, 23·2 Cals. and with 2 litres, 24·6 Cals. (*see* note, p. 568).

The saturated solution of calcium chloride, corresponding with the composition, $CaCl_2 + 6H_2O$, has the specific heat 0·52.

The densities and concentrations of aqueous calcium chloride solutions are as follows:

At 18°		100 grams of solution contain grams of $CaCl_2$	At 18°		100 grams of solution contain grams of $CaCl_2$
Sp. grav.	Degree Bé.		Sp. grav.	Degrees Bé.	
1·00583	0·7	0·854	1·22946	27·0	25·00
1·01292	2·0	1·696	1·29032	32·5	30·70
1·02679	3·5	3·34	1·34857	37·3	35·91
1·04381	5·5	5·34	1·39649	41·0	40·14
1·08659	11·3	10·21	1·43583	43·9	43·61
1·13123	16·7	15·06	1·47300	46·2	46·97
1·17905	21·7	19·99	1·51784	49·2	51·01

[1] TABLE OF FREEZING-POINTS, CONCENTRATIONS, AND SPECIFIC HEATS OF THE VARIOUS SOLUTIONS USED AS BRINE IN FREEZING MACHINES

Sp. gr. of solution at 18°	Degrees Baumé	Freezing-points of the solutions			Grams of the different salts in 100 grams of water for solutions of			Specific heat of the solutions		
		$CaCl_2$	NaCl	$MgCl_2$	$CaCl_2$	NaCl	$MgCl_2$	$CaCl_2$	NaCl	$MgCl_2$
1·00	0	0°	0°	0°	0	0	0	1	1	1
1·02	2·7	− 1	− 2	− 1·7	3·3	3	3	0·96	0·97	0·965
1·04	5·4	− 2·5	− 4·4	− 3·5	6	4·5	5	0·93	0·938	0·93
1·06	8·0	− 3·5	− 6·5	− 5·5	7·5	8	7	0·90	0·91	0·90
1·08	10·6	− 5	− 8·5	− 7·7	10	11	9·5	0·87	0·88	0·87
1·10	13	− 7	− 10·5	− 10	12·5	13	11·5	0·845	0·86	0·84
1·12	15·4	− 8·6	− 12·5	− 12·7	15	16	14	0·82	0·84	0·825
1·14	17·7	− 10·7	− 14	− 15·6	17	18	16	0·796	0·82	0·79
1·16	19·8	− 13	− 16	− 19	18·5	22	18	0·778	0·806	0·77
1·18	22	− 15·5	− 17·6	− 22	21	24	20	0·757	0·793	0·75
1·20	24	− 18·4	− 18	− 26	23	27	22·5	0·743	0·780	0·73

N.B.—Since with calcium and magnesium chlorides it is possible to obtain solutions still more concentrated than 20° Bé., the freezing point may be lowered still further, even to − 30° or below.

75 per cent. of $CaCl_2$ and costs £1 12*s.* to £2 16*s.* per ton. In Italy 3700 tons were produced in 1906, of the value of £13,320; 1035 tons were imported in 1904; 1740 tons, of the value of £5560, in 1908; 1406 tons, of the value of £4501, in 1909; 1514 tons in 1911, 2247 in 1912, 2243 in 1913, 1564 in 1914, 1880 in 1915, and 1158 in 1916. The pure product costs up to £20 per ton, and if it is anhydrous and chemically pure it costs more than £40 per ton.

In 1905 Germany exported 2825 tons, of the value of £5680.

The United States produced 14,606 tons in 1911, and 18,550 tons, at about £1 8*s.* per ton, in 1912.

CALCIUM BROMIDE AND IODIDE : $CaBr_2$ and CaI_2. These salts are similar to the chloride but more deliquescent. By the action of the carbon dioxide of the air on the iodide HI is first separated, and this yields free iodine with the oxygen.

CALCIUM FLUORIDE : CaF_2. This compound is found in nature in colourless cubes or octahedra as *fluorite* or *fluorspar* and is sometimes variously coloured. It is also found in compact amorphous masses, and occurs in small quantities in the bones and teeth. It is formed as a voluminous precipitate from solutions of $CaCl_2$ with solutions of soluble fluorides, or by heating cryolite (Al_2F_6, 6NaF) to redness with calcium carbonate, or by boiling cryolite with milk of lime (*see later*, Cryolite).

It is decomposed only by strong acids such as H_2SO_4; it is insoluble in water, and melts easily at a red heat and is therefore used as a flux in the treatment of ores. It becomes phosphorescent on heating and by the action of direct sunlight.

The crude natural product is sold at £2 16*s.* to £4 per ton; the chemically pure precipitated compound costs more than 5*s.* 7*d.* per kilo. The United States produced about 57,000 tons of fluorspar, of the value of £72,000 in 1905, 46,670 tons in 1908, and 45,800 tons in 1909. England produced 42,483 tons in 1909 and 61,621 in 1910.

CALCIUM HYPOCHLORITE (CHLORIDE OF LIME, BLEACHING POWDER)

This salt has not yet been obtained in the pure state, but chloride of lime, which must not be confused with calcium chloride, contains calcium hypochlorite which has probably the following formula: $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}, H_2O$, as its active ingredient mixed with CaO, $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}, H_2O$; it was first prepared by Tennant in Great Britain in 1798 by saturating lime with gaseous chlorine:

$$2Ca(OH)_2 + 2Cl_2 \rightleftarrows 2H_2O + Ca(OCl)_2 + CaCl_2.$$

That the reaction is reversible is shown by the fact that if the excess of free lime or of calcium chloride is eliminated from chloride of lime, a part of the hypochlorite decomposes with liberation of chlorine, whilst it is rendered more stable by excess of lime or by addition of $CaCl_2$ (which makes the hypochlorite more active).

It is maintained by many that the true composition of chloride of lime is $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}$.

INDUSTRIAL MANUFACTURE OF BLEACHING POWDER. The calcium hydroxide employed for the absorption of the chlorine must be pure and not very moist.[1]

---

[1] This calcium hydroxide is prepared only from very pure limestone, which leaves no residue on treatment with acids, and contains no Mn or Fe; the presence of organic matter is of no consequence because, on burning the limestone to quicklime in kilns this is destroyed. Rich limes, which are slaked more easily, absorb chlorine more easily than poor limes. The slaked lime is sieved with great care and allowed to cool in barrels for some days. Theoretically calcium hydroxide, CaO + H_2O, contains 24·3 per cent. of water, the rest being CaO; practically bleaching powder of good strength is obtained by the employment of a quicklime containing about 2 per cent. to 4 per cent. more than the theoretical quantity of water. Although the maximum strength is obtained by passing very dry chlorine over very dry slaked lime, in practice it is not easy to work under such conditions. A larger quantity of free water in the slaked lime enables it to absorb chlorine very rapidly, but lumps are formed in the mass, and with these the chlorine is unable to react.

The chlorine should not contain HCl as otherwise $CaCl_2$ is formed and renders the bleaching powder deliquescent. The fact must be taken into account that in winter chlorine is dryer than in summer, because a good deal of moisture is deposited in the pipes. The lime is exposed in lead chambers (Fig. 244) 20 to 30 metres long, about 10 metres wide, and 2 metres high, supported by a wooden framework. The floor of the chambers is of asphalt, and 10 kilos of bleaching powder can be produced daily per square metre of surface. These chambers are also constructed of metal, sometimes even of iron, but not of brickwork, as it is necessary to dispel rapidly the heat formed in the chamber during the reaction. Two or three of these chambers are arranged in series in order to enable work to be carried on continuously.

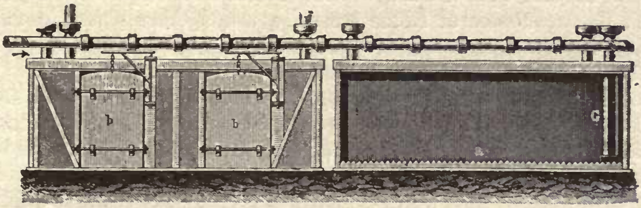


Fig. 244.

The layer of slaked lime, 80 to 100 cm. in depth, should be loosely heaped, and the chlorine which passes in at the top of the chamber rapidly penetrates throughout the mass to the bottom. By watching the process through small windows it is possible to tell by the more or less greenish colour of the gas whether the lime is still absorbing chlorine. Generally saturation is complete in twenty-four hours. Before opening the chamber it is connected for twelve hours with the works chimney, and air is thus carried through it in order to remove all excess of chlorine. If the product has not a strength of 35 to 36 per cent. of active chlorine the mass is remixed with shovels and treated with chlorine once more.

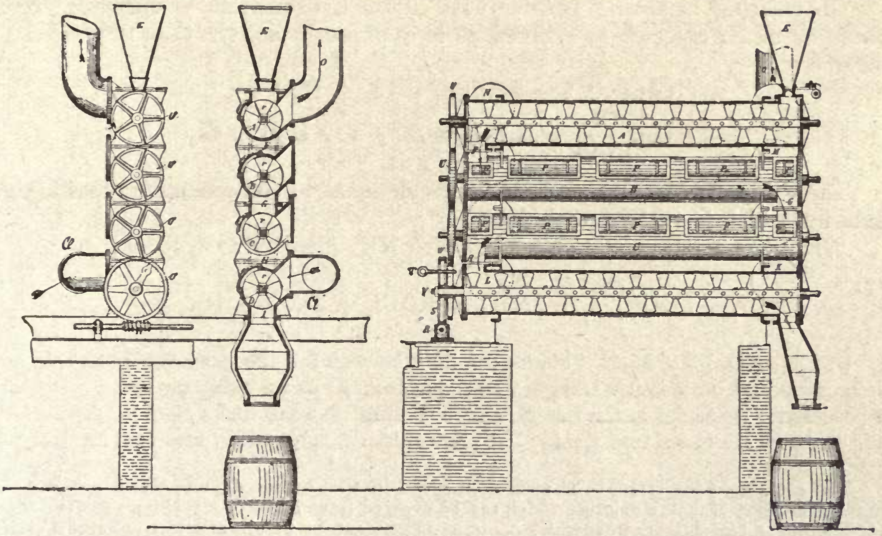


Fig. 245.

In order to accelerate the absorption of the chlorine and to avoid serious injury to the workmen discharging the bleaching powder from the chamber, and also to eliminate danger of explosion in case the electrolytic chlorine used is contaminated with hydrogen and thus gives an explosive mixture in the absorption chamber (*see* p. 150), various forms of plant have been proposed, of which the most practical and efficacious is that of Hasenclever (1891), Fig. 245. This consists of four superposed leaden cylinders 2 to 3 metres long, furnished with stirrers, *A*, which continuously transport the lime which falls from a hopper, *E*, successively from one cylinder to the next below it.

At the same time chlorine enters through a wide lower tube, *Cl*, and traverses the cylinders in the opposite direction to the lime. The chlorine is completely absorbed in the upper cylinder where the fresh lime enters, very little passing up the exit flue, *o*. In the lower part of the plant there is a discharge outlet for the saturated bleaching powder, which is at once collected in barrels. The workmen who handle bleaching powder smear their bodies with fat and wear a mask which protects their respiratory organs and eyes.

The Società Elettrochimica of Rome are using ten of these plants in their works at Bussi.

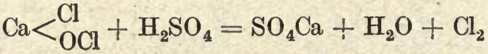
Most of the bleaching powder now made is produced in electrolytic alkali works in order to utilise the large quantities of chlorine which they obtain. In 1907 (Fr. Pat. 370,873) the Elektron works at Griesheim produced bleaching powder containing 80 to 90 per cent. of active chlorine, by almost completely saturating milk of lime with chlorine and continuing to stir it; after filtration the liquid is slowly evaporated *in vacuo* and thus a solid chloride of lime is obtained which is more stable and purer than the ordinary product and is soluble in water.

Commercial bleaching powder is a soft white powder with an odour of chlorine, and its aqueous solution has an alkaline reaction and is a strong bleaching agent. It is decomposed by the air through the action of the carbon dioxide.

It also decomposes slowly in closed vessels with formation of oxygen, and this change is more rapid under the influence of sunlight and of heat. In some cases closed vessels in which it is contained may even explode. In order to store bleaching powder without danger it is kept in wooden vats in the dark for some time after it has been prepared. Barrels containing bleaching powder should not be sealed hermetically, and should be kept in well-ventilated dark store-rooms.

On treating bleaching powder with dilute hydrochloric or sulphuric acid, twice as much chlorine is evolved as is apparently active, that is, united to oxygen:

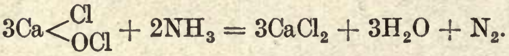
$$CaCl \cdot OCl + 2HCl = CaCl_2 + H_2O + Cl_2$$



$$Ca{<}\begin{smallmatrix}Cl\\ OCl\end{smallmatrix} + H_2SO_4 = SO_4Ca + H_2O + Cl_2$$

The value of bleaching powder is proportional to the amount of this active chlorine which is evolved with acids.[1]

When bleaching powder is heated with NH_3 nitrogen is evolved:



$$3Ca{<}\begin{smallmatrix}Cl\\ OCl\end{smallmatrix} + 2NH_3 = 3CaCl_2 + 3H_2O + N_2.$$

USES AND PRICES.. Chloride of lime is used for the preparation of chlorine, chloroform and oxygen (*see* Oxygen), as a disinfectant, as an oxidising agent, and more especially for bleaching cotton fabrics, and in printing on wool, which more readily absorbs the dyestuffs after such treatment. The price of bleaching powder varies with its strength,

---

[1] In commerce the strength is also often given in Gay-Lussac degrees which indicate the number of litres of active chlorine which can be evolved from 1 kilo of bleaching powder; thus, for example, a bleaching powder which contains 25 per cent. by weight of active chlorine is called 79° Gay-Lussac; if it contains 40 per cent. of active chlorine it is of 126° Gay-Lussac, because 1 kilo of this bleaching powder would evolve 400 grms. of chlorine and a litre of the gas weighs 3·16 grms., and $\frac{400}{3 \cdot 16} = 126°$.

The strength of bleaching powder is determined with $\frac{N}{10}$ solution of sodium arsenite obtained by dissolving 4·950 grms. of pure As_2O_3 in 200 c.c. of water and 20 grms. of pure sodium bicarbonate; the whole is boiled with stirring, allowed to cool, and made up to 1 litre; 1 c.c. of this solution corresponds with 0·00355 grm. of active chlorine. The titration is carried out by stirring up 7·1 grms. of the well-mixed bleaching powder to a paste with water, diluting with water to 1 litre, shaking well, and immediately removing 50 c.c. (= 0·355 grm.) of the sample; this is titrated in a beaker with the solution of the arsenite, the end of the operation being detected by spotting the liquid on to filter-paper impregnated with starch and potassium iodide solution until the blue spot produced by iodine liberated by the chlorine is no longer obtained.

and for a strength of 35 per cent. chlorine may reach £8 per ton. In 1906, when the European syndicate which fixed the prices ceased to exist, the price fell to £1 4*s.* per ton, and in Italy, where the two existing works enjoy the advantage of a protective tariff of £1 16*s.* per ton, the price rose again to £5 12*s.* and £6, and it is gradually rising in other countries.

The world's production of bleaching powder in 1904 was 260,000 tons and now exceeds 350,000 tons.[1]

CALCIUM NITRATE: $Ca(NO_3)_2$ (crystallising with $4H_2O$). On treating of potassium nitrate we mentioned that the nitrogen of putrefied organic matter was oxidised in presence of lime by certain nitrifying bacteria which transformed it into calcium nitrate; this is often found as an efflorescence on the walls of stables.

It is very soluble in water and in alcohol and is readily transformed into potassium nitrate by potassium salts. It is abundant, naturally formed, in Venezuela and is an excellent manure. When purified it is used for incandescent mantles.

The crude product used as a fertiliser is as efficacious as sodium nitrate, and since it has been obtained electrically from atmospheric nitrogen (p. 350) it is sold at less than £8 per ton; chemically pure for incandescent lighting it costs 1*s.* 6*d.* per kilo. The exportation of calcium nitrate from Norway and the local consumption for agricultural purposes have progressed as follows (tons):

Year . .	1905	1906	1907	1908	1909	1910	1911	1912	1913	1915	1916
Exports . .	115	589	1344	7053	9422	1353	120,000	52,000	70,900	38,609	46,000
Consumption .	—	—	215	—	970	—	1937	—	5500	8000	—

In Norway a further quantity of about 3000 tons per annum is consumed.

BASIC CALCIUM NITRATE is less deliquescent, and contains about 13 per cent. of nitrogen, 26 per cent. of lime, and 24 per cent. of water, together with very small amounts of nitrites (which are sometimes harmful to vegetation). It is used as a synthetic nitrogenous fertiliser (*see above* and p. 396).

CALCIUM NITRITE: $Ca(NO_2)_2$, is produced together with calcium nitrate in the electric processes for the utilisation of atmospheric nitrogen (*see* p. 396); in order to separate it the solution is concentrated until on cooling to 30° to 35° crystals of the nitrite are deposited, whilst the nitrate remains in solution.

According to Ger. Pat. 220,539 of 1909, the nitrite may be transformed into nitrate by heating it to over 300° in presence of NO_2: $Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO$; the nitric oxide is mixed with the necessary quantity of air to retransform it into NO_2 and then re-enters the cycle. In a similar manner nitric acid may be obtained from the mixture of nitrates and nitrites.

CALCIUM SULPHIDE. This is a yellowish mass which is obtained on heating calcium sulphate with charcoal. The sulphate is reduced more easily by CO, and reduction then begins at 680° and finishes at 850°, whereas with carbon it commences only at 700° and ends at

---

[1] The output of chloride of lime (tons) in different countries, etc., is as follows:

Country		1902	1904	1906	1908	1910	1911	1912	1913	1914	1915
Italy	production	—	4,000	5,000	—	—	8,746	8,755	8,234	9511	9611
	imports	10,000	6,000	5,200	2,940	3,784	3,832	3,472	2,642	2515	773
	exports	—	—	—	1,190	461	865	424	708	280	265
Germany	production	—	81,000	—	—	100,000	—	—	—	—	—
	imports	—	320	1,600	1,465	1,266	1,080	—	—	—	—
	exports	—	30,000	28,000	23,900	24,716	27,100	32,084	—	—	—
England	production	—	190,000	—	—	—	—	—	—	—	—
	imports	—	—	—	—	—	—	—	—	—	—
	exports	50,000	—	—	37,000	50,000	—	46,000	—	—	—
France	production	—	40,000	—	—	—	45,000	—	—	—	—
	imports	—	—	—	—	—	—	—	—	—	—
	exports	—	—	—	—	11,700	13,200	—	12,620	—	—
Austria	production	—	—	—	—	—	—	18,000	—	—	—
	imports	—	2,400	—	—	—	—	—	—	—	—
Russia	production	10,000	—	—	12,000	21,000	—	24,600	—	—	—
	imports	—	—	—	—	350	—	300	—	—	—
Spain	production	—	—	—	—	—	—	—	—	—	—
	imports	—	—	—	2,500	2,300	—	—	—	—	—
United States	production	—	—	—	—	70,000	—	—	—	—	—
	imports	65,000	—	50,000	36,000	50,000	40,000	50,000	—	—	—
Canada imports .		—	—	—	—	—	—	4,817	—	—	—
Japan production .		—	—	—	—	—	—	17,000	—	—	—
World's production .		—	260,000	—	—	300,000	—	—	350,000	—	—

1000°. Between 700° and 800° the reaction is as follows: $CaSO_4 + 2C = CaS + 2CO_2$, but between 800° and 1000°, $CaSO_4 + 4C = CaS + 4CO$. When dissolved in water it gives *calcium hydrosulphide*, $Ca(SH)_2$. When quite pure and dry it is not phosphorescent, but is rendered so by traces of certain salts.

CALCIUM SULPHITE and BISULPHITE: $CaSO_3$ and $Ca(SO_3H)_2$. These compounds are obtained by the action of SO_2 on slaked lime and on milk of lime in wooden chambers or boxes.

The SO_2 fumes are passed in at the bottom of a tower which contains limestone (calcium carbonate) and down which a shower of water falls from above. A solution of calcium sulphite is so formed and collects at the bottom of the tower, carbon dioxide only escaping at the top.

Calcium sulphite is solid and forms a readily transportable source of SO_2, which can be regenerated from it by the action of acids. It is insoluble in water, but readily soluble in aqueous SO_2, forming calcium bisulphite.

The bisulphite is used in large quantities in cellulose works and paper-mills, also in sugar factories, spirit distilleries, and breweries, as an antiseptic, etc. U.S. Pats. 84,698 of 1907 and 945,426 of 1908 describe two forms of industrial plant for the manufacture of calcium bisulphite.

Neutral commercial calcium sulphite costs £18 per ton and the purified product £26 per ton. The bisulphite in solutions of 13° to 14° Bé. costs £6 per ton. In 1909 Italy produced 200 tons of calcium sulphite.

CALCIUM SULPHATE: $CaSO_4$

This compound is found abundantly in nature without water of crystallisation as *anhydrite*, of sp. gr. 2·96, in shining, lamellar masses, often pink or red or bluish (*vulpinite*, found at Vulpino near Bergamo). It occurs also with $2H_2O$ in large monoclinic prisms of sp. gr. 2·32 or as a granular crystalline mass known as *gypsum*; when this forms large transparent rhomboidal prisms, sometimes united in pairs in the shape of a V, cleaving into leaflets, it is called *selenite* and is used in optical instruments. Selenite is not very hard (2·5 on Mohs' scale) and has sp. gr. 2·3. When gypsum occurs in compact masses with granular (saccharoid) fracture like marble, it is termed *alabaster* (or *gypseous alabaster*). *Fibrous gypsum*, with a silky aspect, is also found, and in some localities it occurs combined with sodium sulphate as *glauberite*, $CaSO_4$, Na_2SO_4.

The gypsum obtained on precipitating a soluble calcium salt with sulphuric acid crystallises with $2H_2O$; it is very slightly soluble in water (1 part in 450 parts both at 0° and 100°), and acquires its greatest solubility at 35°, namely, 2·5 grms. per litre. The solubility in water increases with the fineness of the gypsum and is diminished by the presence of salts with an ion common to the gypsum (calcium salts and sulphates); by other salts the solubility is increased, since by double decomposition small amounts of other undissociated calcium salts are formed, this being especially the case with solutions of the alkali chlorides.

Gypsum is markedly soluble in acids: 100 grms. of 90 per cent. sulphuric acid dissolve 2 grms. of $CaSO_4$ and 100 grms. of the fuming acid, 10 grms.; 1 litre of seminormal HCl, 7·61 mgrms. (HNO_3 9·27 mgrms.); 1 litre of normal HCl, 11·51 mgrms. (HNO_3, 13·1 mgrms.); 1 litre of the 2*N*-acid, 15·75 (20·4) mgrms. and 1 litre of 10*N*-acid, 23 (23·4) mgrms.; 1000 grms. of glycerine dissolve 1 grm. of $CaSO_4$. Natural anhydrite behaves like gypsum deprived of its water, that is, it does not set with water. When calcium sulphate is heated with water in a sealed tube at 150° and then cooled, large crystals, $CaSO_4, 0{\cdot}5H_2O$, are formed, these being obtained also when ammonium nitrate is prepared by treating calcium nitrate with ammonium sulphate in an autoclave at 150°.

When natural gypsum is heated to 107° to 130° it loses a considerable part of its water (forming $2CaSO_4, H_2O$, which contains 6·2 per cent. of water and has sp. gr. 2·44), and this product has the valuable property, when worked to a paste with water, of recombining with the whole of its water of crystallisation, and immediately becoming very hard with separation of the excess of water; for this reason it is used for very varied industrial and artistic purposes. If, however, it is heated to 170° it loses all its water of crystallisation, and also its property of hardening when mixed with water, and is then known as *dead-burnt* or *overburnt* plaster. If heated beyond 1000°, best at 1200° to 1300° (some maintain that 400° is sufficient), it yields *gypsum for pavements* (made up to a paste with glue it gives compact, shiny pavements), which would be a basic calcium sulphate, since at the above temperature a little of the lime (up to 3 per cent.) is set free. To retard the rapidity of setting and hardening of gypsum, the latter may be mixed with 0·1 to 0·5 per cent. of sodium phosphate. The phenomenon of the setting of gypsum was studied as early as 1765 by Lavoisier but more rationally by van't Hoff and his pupils in 1900–1903. It is now held that the burnt gypsum and the small amount of overburnt gypsum always present are more soluble in water than the dihydrate ($2H_2O$), so that mixing with water results in the formation of a supersaturated solution of the sulphate from which the hydrated gypsum separates as a mass of acicular crystals, these hardening rapidly with slight heating and diminution and then increase in volume (1 per cent.); the sharpness of the finest details of gypsum casts is thus explained. In setting gypsum absorbs more water than corresponds with the $1\frac{1}{2}$ mols. necessary to give the dihydrate, the excess of water remaining included and rendering the gypsum less compact and less resistant to weathering. The resultant hardness and the rapidity of setting are the less, the greater the quantity of water used (generally 1 part of gypsum and 1 part of water; for casts, more water is taken, *see later*). Gypsum for paving (*see above*) sets more slowly (some days, instead of half an hour as with the hemihydrate), but becomes harder than ordinary gypsum and resists weathering better, perhaps because it contains less included water; it may also be used for external decorations.

On a small scale plaster of Paris is prepared by gradually heating the natural powdered gypsum in iron pans with continuous stirring until water is no longer condensed on the cover of the pan.

On a large scale it is heated in large ovens similar to those used for baking bread, out of contact with the products of combustion. The furnace is heated with wood and coal up to a suitable temperature and the fuel removed before the gypsum is introduced. Gas-fired furnaces are also used, and at present metallic drums heated by a current of hot air are coming into use.

The burning of crude gypsum takes from twelve to twenty-four hours; 60 to 70 kilos of coke are used for heating per cubic metre of plaster of Paris produced. In modern furnaces, for example, of the Perin type, 27·5 kilos of coke are used per 1000 kilos of gypsum, starting from crude gypsum with 22 per cent. of water and finally obtaining plaster of Paris containing 6·2 to 7·70 per cent. of water.[1]

A method of manufacture which is often adopted is the following: The natural gypsum, in large lumps as it is quarried, is first crushed and then ground in the usual form of mill with horizontal stones.

After grinding in this way the crude gypsum is heated in open iron pans furnished with stirrers and holding about 60 to 70 kilos. These pans are arranged over a hearth heated with coal and lined with refractory bricks in order to avoid direct contact with the flame or with the hot gases; in this way heat is transmitted through the refractory lining and

---

[1] In a gypsum works producing 2500 kilos of burnt gypsum per hour, the mean consumption of coke was 100 kilos (*i. e.*, 4 per cent.) per hour, the loss of heat per hour being calculated as follows: 38,532 Cals. carried away by the air, 272,955 to evaporate the water of the gypsum, 67,513 for the chemical transformation, 113,322 to heat the gypsum (spec. heat 0·273), 18,603 radiated and dispersed from the whole surface (95 sq. metres) of the furnace and lost in various secondary ways.

the temperature of the mass of gypsum does not exceed 120° to 130°; 18 to 20 kilos of coal are used per 100 kilos of gypsum.

During heating the stirrer is always kept in slow motion and the end of the process is recognised by the fact that the mass ceases to "boil," because no more steam is evolved in the form of vapour jets which rise through the powdered gypsum.

"*Scagliola*" is thus obtained; in order to obtain ordinary plaster of Paris the gypsum is heated in small pieces in furnaces without stirrers, but a poorer quality is thus obtained; this process takes a few hours.

Dead-burnt plaster may apparently be partially regenerated by the addition of about 4 per cent. of sodium bisulphate.

It appears that when the gypsum is removed from the ovens it contains no water and absorbs only 7 to 8 per cent. on standing in the air. It has then the power of setting, which may be accelerated by addition of 5 to 10 per cent. of powdered limestone, or retarded by 2 to 5 per cent. of CaO or by borax, glue, dead gypsum or alum solution.

Gypsum is used for making models of artistic figures by using a paste of 1 part of gypsum and 2½ parts of water, because it reproduces even the finest details; it is used for modelling, etc.

It is used as a corrective for certain soils and also diminishes the loss of ammonia from stable manure by converting the somewhat volatile ammonium carbonate into calcium carbonate (less soluble than $CaSO_4$) and non-volatile ammonium sulphate.

Gypsum obtained chemically by precipitation forms very fine powder and may be used as a loading for paper.

Treatment of gypsum with a solution of glue and a little zinc sulphate yields *stucco*, which is used for ornamentation and sets more slowly but more strongly than gypsum alone. When moistened with a hot solution of alum, gypsum yields *alumed gypsum* or *English cement*, which is hard like marble.

STATISTICS AND PRICES. In Italy, 264,843 tons of gypsum, valued at £97,160, were produced in 1890 and 341,883 tons in 1902, besides 270 tons of calcium sulphate as a chemical product.

Germany imported 11,285 tons of gypsum in 1909, 10,873 in 1910, 11,973 in 1911, 10,627 in 1912, and 8818 in 1913, the exports being 63,220 tons in 1909, 89,660 in 1910, 102,754 in 1911, 108,137 in 1912, and 132,693 in 1913. France produced 1,316,500 tons in 1907; in 1903 390,000 cu. metres of gypsum were consumed in Paris. England produced 194,000 tons in 1908 and 255,560 in 1910, and Canada 346,500 tons. The United States produced 400,000 tons in 1900, 1,694,000 in 1908, and 2,150,000 (£1,240,000) in 1911; in 1901 3156 tons of burnt gypsum and 240,000 tons of crude gypsum were imported into the United States. The price of burnt gypsum varies from 14*s.* 5*d.* to 24*s.* per ton, while commercial precipitated calcium sulphate costs £14 per ton.

CALCIUM SILICATE : $CaSiO_3$

This compound is found pure and crystalline as *wollastonite*, $CaSiO_3$, a mineral which is not very abundant. Calcium silicate is an important constituent of the natural silicates which abound in many minerals and geological formations. Since a remote epoch it has been used as a constituent of glass, and it is specially in connection with this substance that calcium silicate is of great importance to us.

GLASS[1] consists of an amorphous transparent mixture of silicates of the alkali, alkaline earth and heavy metals.

---

[1] Glass is of very ancient origin: the Egyptians were well acquainted with its production and working in 1800 B.C., and perhaps the Chinese manufactured glass at a still earlier date. The art of melting and blowing glass passed from the Egyptians to the Phœnicians and then to the Ancient Romans (200 B.C.), who used it for artistic objects. The glass industry then developed at Byzantium and later in Venice, where it acquired great importance. Glass mirrors have been manufactured since 1400; before that time metallic mirrors were used. In Bohemia the glass industry developed in the Middle Ages, then declined, and reacquired great importance during the past century. In the tenth century stained glass for windows, especially in churches, already occurs. In France and in England the glass industry became important towards the end of the Middle Ages, and the large works at the Faubourg St. Antoine in Paris were founded in 1800 and were afterwards removed to St. Gobain. In Germany the industry received a great impetus through the introduction of the Siemens furnace. The mirror industry developed in

The modern and scientific definition of a glass takes no account of its chemical composition and includes any substance obtained from the solidification of a fused mass by a slow, gradual process yielding an amorphous solid. It has, therefore, no sharp solidification point (characteristic of crystallised substances), but passes gradually into the solid or molten condition. If account were to be taken of the chemical composition, it would be difficult to include in the definition modern pure quartz glasses.

Glasses are divided into the following principal groups:

I. **Glasses consisting of Calcium and Potassium Silicates.** These are very hard, not very fusible, and very resistant to the action of water and acids. They are completely colourless and are used for the preparation of chemical and physical apparatus. They have a specific gravity of about 2·40.

II. **Glasses consisting of Calcium and Sodium Silicates.** These are more fusible and less resistant than those of the preceding class; they resist the solvent action of water and of acids. They are used for making ordinary sheets and cheap objects, and have always a slight bluish-green colour and a specific gravity of about 2·65. Mirrors are often made of a mixture of glasses of groups I. and II.

III. **Glasses composed of Lead and Potassium Silicates.** These are readily fusible and are suitable for many ornamental objects. They have a high specific gravity, possess marked lustre, and refract light very strongly.

They are used in the preparation of so-called *crystal glass* of sp. gr. 2·9 to 3·25 and also form *flint glass* of sp. gr. 3·3 to 3·6, in which considerable quantities of boric acid and bismuth are added to the lead silicate. The *paste* (strass) used for the manufacture of artificial gems is very refractive and transparent and belongs to this group.

Lead glasses are used for lenses and optical apparatus, but these are now also prepared with barium, as they are then harder, although still highly refractive. *Crown glass* for optical purposes has the refractive index 1·50 to 1·56 and does not contain lead.

IV. **Common Bottle Glasses.** These consist of silicates of sodium, potassium, calcium, and aluminium accompanied by iron, manganese, and sometimes by magnesium. They have sp. gr. 2·73, contain less alkali than other glasses, and have a yellow or dark green colour.

V. **White, Opaque or Translucent Glasses,** as used, for example, for lampshades, are obtained by addition of barium sulphate, bone-ash (tricalcium phosphate), etc. As *smalts* are known, besides certain semi-transparent and coloured glasses, also those made from plumbiferous glass rendered opaque by oxide of tin. Bottle glass to resist rapid

---

Austria in 1700 and in Germany only after 1850. Various attempts to revive this industry in Venice at the beginning of the nineteenth century were unsuccessful and the actual revival of glass-working at Murano (near Venice) is largely due to Dr. Salviati, who, by investigating with an enlightened mind the good points of the old processes and bringing them into harmony with modern science and industry in the middle of the nineteenth century, was able to revitalise the new works, which once more gained the admiration of foreigners for the intelligent work of the men able to shape in a thousand fashions and with exquisite artistic taste the soft formless molten metal drawn from the red-hot furnaces.

The Venetian renaissance was completed in its most highly artistic forms by the remarkable ability of Luigi Lobmeyer (born at Vienna in 1829), who succeeded in creating an entirely new art of cutting and polishing glass with such refined taste that in a very short time he claimed the attention of the whole world by the industrial production of beautiful artistic objects.

In the nineteenth century the glass industry acquired a new impetus amongst all civilised nations, when it became possible not only to produce artistic objects for the wealthy, but also such as could be made cheaply and on a large scale.

The large modern glass industry has been enabled to arise through the valuable assistance of chemistry and engineering. By means of the first the composition of the necessary "batches" for obtaining the most varied qualities of glass with precision and security was studied; and the second furnished the necessary means for the large-scale mechanical production. The exact relations between the prime materials, quartz, silicates, sodium and potassium carbonates, sodium sulphate, lime, lead oxide, etc., and carefully regulated temperatures allow the various types of glass to be obtained with certainty.

The old glass-melting furnaces yielded a very impure glass, and the heating was not so regular as in modern furnaces using special hearths with suitable draught, aided by powerful fans and fed by fuel of the first quality. Excessive consumption of fuel and results which are often unsatisfactory, render the success of important enterprises very difficult.

changes of temperature, such as is used for bottles in which beer, wine, milk, etc., are to be sterilised, is rich in SiO_2 and poor in alkali.[1]

VI. Coloured Glasses. A *yellow* colour is obtained by addition of oxide or salt of antimony, or oxide of iron, silver or uranium; *red* by gold chloride, red ochre, cuprous oxide or selenium; *green* by ferrous, copper or chromium oxide; *blue* by cobaltous oxide, or traces of copper for glass rich in alkali and lime. Such colours are often due to the separation of the respective metals in the colloidal state, the glass serving as solid solvent; with selenium Fenaroli (1913) showed this to be present as submicrons of selenium not more than 40 $\mu\mu$ in dimensions, or in some cases of polyselenides. *Iridescent* glasses are obtained by the action of vapours of metallic chlorides on hot glass and *nacreous* glass by addition of scales of mica.

VII. Pure Quartz Glass. By definition glass is an amorphous mass, whereas quartz is pure crystallised silica, so that this material is more correctly called *pure silica glass* (SiO_2), as it constitutes an amorphous (vitreous) modification of silica and is hence not quartz. In 1839 Gaudin found that vitreous silica is optically inactive, and both he and also Gautier in 1869, and better in 1878, prepared various small objects of fused quartz (beads, capillary tubes, spirals, etc.). Boys in 1889 indicated the importance of quartz glass. Only after 1901 was Shenstone able to prepare fairly large apparatus and tubes, and in 1902 Heraeus (Ger. Pat. 175,385) succeeded in melting quartz in iridium crucibles with the oxy-hydrogen blowpipe. At the same time Schott & Co. of Jena obtained common objects of transparent quartz with the help of the electric furnace. In 1902–1903 Völker in Germany, Bottomley in England and Hutton in America succeeded in making industrial apparatus and objects by comparatively cheap processes, although this glass was opaque owing to the inclusion of numerous air bubbles. The fusion cannot be carried out in crucibles of carbon (free Si would then form) or of CaO or Al_2O_3, as these would unite with the fused quartz. Heraeus (Ger. Pat. 179,570) uses crucibles made with zirconium oxide, those of iridium being spoiled at each operation.

Quartz is transformed into a fused glass at 1700°, but the necessary fluidity is attained at 1850°, or, for blowing certain objects, 2000° (with considerable vaporisation of the SiO_2). Quartz expands regularly up to 570°, the dilatation then suddenly doubling and the mass becoming cracked and splintered, but the numerous splinters remain united and fuse together only at a higher temperature, since above 1000° the expansion is almost uniform. After innumerable technical difficulties and serious failures, it is now possible to prepare the most varied articles of small dimensions and even large dishes (up to 50 cm. in diameter) and large coils with tubes 810 cm. wide. Transparent quartz apparatus costs from three to twenty times as much as the opaque variety [Ger. Pats. 169,958, 170,234, 174,509; Eng. Pats. 10,670 and 18,434 (1909) of the Thermal Syndicate and 18,713 (1909); also Ger. Pat. 204,854].

This glass is obtained from very pure silica or quartz containing 99·5 per cent. of SiO_2. It is absolutely unattacked by acids and neutral substances (excepting hydrofluoric acid, phosphoric acid and magnesium ammonium phosphates), but is acted on by alkalies and metallic oxides (at high temperatures). Above 1000° the glass becomes slightly porous towards hydrogen. The most striking characteristic of quartz glass is its very low coefficient of expansion, which at 1000° is seventeen times smaller than that of platinum; for this reason it may be immersed red-hot into cold water without breaking. Quartz thermometers heated repeatedly and for a long time at 750° undergo no displacement of the zero, this being unattainable with other thermometers (*see later*).

At 1500° quartz glass begins to become plastic, while prolonged heating at 1200° produces devitrification owing to formation of crystoballite or tridymite, the density increasing at the same time. Impurities facilitate devitrification.

It is a good electrical insulator even at high temperatures. The density of transparent quartz glass is 2·21 to 2·22 and that of the opaque form 2·07; the refractive index for the D line is 1·4585 and the dispersion between the C and F lines, 0·00676. It allows ultraviolet rays to pass through it easily (especially the glass of uviol lamps, *see* p. 238).

Glass is amorphous and a bad conductor of heat. The amorphous condition is

---

[1] Glasses rich in alkali are fragile and little resistant to pressure, but since those rich in silica are harder, fusion to obtain a homogeneous mass is conveniently effected in tank furnaces. Bottles for pasteurisation should have uniformly thick walls and hence should be machine- and not mouth-blown; careful and gradual cooling is also necessary.

characteristic for glass and is obtained rarely with simple silicates but easily with complex silicates, especially those rich in silica. The most stable form of the silicates is the crystalline, which is derived from amorphous glass when this is kept for a long time at the temperature of incipient softening (devitrification).

The composition of glasses ordinarily varies within the following limits :

$$K_2O, CaO, 6SiO_2 \text{ and } 5K_2O, 7CaO, 36SiO_2;$$

the K may be replaced by Na and the Ca by Pb.

Good glasses for chemical purposes ordinarily contain so much silica that a trisilicate is formed, and the following proportions give good results : $1{\cdot}34K_2O + 1CaO + 7SiO_2$. Zulkowski maintains (1899) that glass is a true chemical compound, which he supposes to be a double silicate of the general formula $Si_nO_{2n-1}\left<\begin{matrix}OM'\ M'\ O\\O\text{—}MO''\text{—}\end{matrix}\right>Si_nO_{2n-1}$, where M′ is the alkali metal and M″ the divalent metal Ca, Pb, etc.[1]

A good glass should be resistant to the action of the atmosphere, water, carbon dioxide, acids and dilute alkalis. Glasses rich in alkali are attacked more easily by water than those containing lead; boiling water and particularly steam vigorously attack ordinary glasses, whereas acids are almost without action. No quality of glass, however, is absolutely resistant. Even in the air glasses lose their transparency and become dull in time, because alkali is dissolved. A good glass should resist the action of strong HCl vapours for twenty-four hours. The resistance increases with increasing amounts of SiO_2, though this constituent must not exceed 80 per cent. on account of the infusibility and brittleness of the resultant glass. For equal contents of silica, that glass which contains the most lime and the least alkali is most resistant. The coefficient of dilatation increases with increasing amounts of alkali. The specific gravity is about 2·48,[2] and the mean coefficient of absolute thermal conductivity K = 0·0022.

The coefficient of linear expansion of glass varies with the quality and is 0·000008613 to 0·000008969 for ordinary and mirror glass and 0·000008167 for flint glass; the coefficient of cubical expansion is 0·000025839 for soda glass, 0·00002285 for potash glass, 0·00002431 to 0·00002758 for window glass and 0·00002280 for crystal glass, but the value is changed somewhat if the glass is kept at a high temperature for a long time. This explains why thermometers not made from normal glass may undergo displacement of their scale by several degrees after prolonged use; the greatest variations are obtained with glass containing potash and soda, the least with those containing either potash alone or soda with lime and alumina. A good composition for normal thermometer

---

[1] We here give the percentage composition of certain glasses of various qualities and also of various epochs:

	SiO_2	Na_2O	PbO	CaO	$Al_2O_3 + Fe_2O_3$	MgO	MnO
Mirror glass from St. Gobain	73	11·5	—	15·5	0·8	—	—
Window glass	69–71	11·17	—	10–13·5	2·7	—	—
Common green bottle glass	63·5	9·5 (+ 1·3 K_2O)	—	14	5	4·0	3·0
Bohemian glass tubes	74·4	18·5 (K_2O)	—	7·2	0·5	—	—
Brown glass rods from Ancient Egypt	66·0	22·3	—	8·4	2·4	—	0·9
Crystal	50–61	6–11 (K_2O)	28–38	(2)	(0·6–0·9)	—	0·5
Strass	31·2 2·8 (borax)	12 (K_2O)	53	—	1 (Al_2O_3)	—	—
Flint glass	42–45	7–12 (K_2O)	43–51	0·2–0·5	0·7–1 (Al_2O_3)	—	—

[2] The occurrence of *barium* in a glass increases the density, tenacity, lustre, refraction and elasticity, but heightens the resistance towards chemical reagents less than calcium. *Zinc oxide* increases the mechanical and chemical resistance and the refraction, but diminishes the optical dispersion and the thermal expansion. *Magnesia* is not injurious if present to less than 10 per cent. *Alumina* in due proportions gives a glass which is less fusible and more resistant to chemical reagents and to devitrification; it is added as felspar or hydroxide, or for dark glasses as basalt or granite. Boric acid (less than 15 per cent.) increases the refractive index, the chemical resistance and the hardness, but lowers the coefficient of expansion and the melting point. In the proportion $B_2O_3 : 2(-\ 2{\cdot}2)\ SiO_2$ it greatly diminishes the solubility in water.

glass is: 67 per cent. SiO_2, 2 per cent. boric acid, 7 per cent. lime, 7 per cent. zinc oxide, 2·5 per cent. alumina and 14·5 per cent. soda; the thermometer tubes are kept for some days at a high temperature and are then allowed to cool very slowly and finally graduated.

This *normal glass* is prepared especially at Jena and serves also for the manufacture of other chemical apparatus. Another and still better normal Jena glass, with a coefficient of cubical expansion only 0·0000177, contains 72 per cent. of SiO_2, 12 per cent. B_2O_3, 11 per cent. Na_2O, and 5 per cent. Al_2O_3, and may be used for thermometers reading to 500°.

The refractive index of flint glass for yellow light varies from 1·524 to 1·750 according to the lead content, while that of mirror glass is 1·524 and that of crown glass 1·526 to 1·529.

The great resistance of Bohemian glass is due largely to its high content of silica, as well as to the presence of potassium instead of sodium salts. Bluish-green glass, containing much ferrous oxide, only allows very small quantities of thermal rays to pass.

The properties of glass and the constancy of the different types depend, as well as on the chemical composition, also in large part on the mechanical treatment. Glass is of constant type if prepared with furnaces of similar forms and with the same duration of fusion; the order in which the various additions are made to the fused mass should always be the same, and the quality of the fuel also is of great importance.

Sudden cooling renders it brittle but very hard, whilst too slow cooling renders it elastic.[1] By cooling molten glass by immersion in oil or resin, as was proposed by De la Bastia in 1874, or by compressing it between very cold iron plates, as proposed by Fr. Siemens, extremely hard glass is obtained which resists the strongest impacts and may be used for pavements or for street lamps. The hardness of glass increases with its silica content; the hardest glasses are potash glasses, then come soda and finally lead glasses; he hardness is greater at the surface than inside. The resistance to breaking by compression is 161 kilos per sq. cm. for flint glass, 179·5 for crown glass, and 203 for green glass.

PRIME MATERIALS FOR GLASS MANUFACTURE. (1) **Silica.** This is ordinarily employed in the form of quartz, flint pebbles, or siliceous sand. When pure colourless glasses are required, the sand should not contain iron, but if this is present in small amount it sometimes pays to eliminate it by washing or digesting with dilute hydrochloric acid.[2] The quartz and flint are first heated to redness in a furnace to render them friable and are then powdered. For ordinary glasses common sand is used even if it contains clay, as the mass melts the more easily.

(2) **Alkali.** In the past potassium carbonate or plant ashes were almost exclusively employed, and then anhydrous sodium carbonate (Leblanc soda ash) was introduced and became general. Since 1840, however, through the initiative of Baader di Monaco, sodium sulphate obtained directly in the Leblanc process has been in use and has spread greatly of late years. This product is lower in price than soda and can replace it very well if 6 to 7 per cent. of coal is mixed with it (not more, since then sodium sulphide is formed in the furnace and colours the glass brown, this requiring correction with an oxidising agent), and at high temperatures it is decomposed by the silica. All the sulphur of the sulphate escapes as sulphur dioxide, which is lost because it is mixed with large quantities of furnace gases.[3]

---

[1] During irregular cooling internal stresses develop which render the glass brittle and are detectable by birefraction of the glass at certain points. Glasses with strong internal stresses tend to lose them in time, whilst lesser stresses tend to increase.

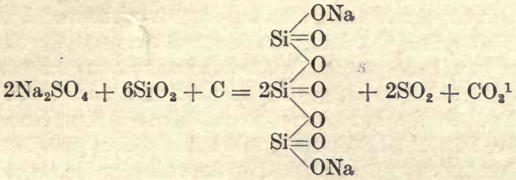
[2] The percentage composition of certain pure sands (from Aquisgrana and Australia) is as follows: SiO_2, 99·7; CaO, 0·1; MgO, 0·06 and $Al_2O_3 + Fe_2O_3$, 0·09.

Sands for common glasses contain more than 96·5 per cent. SiO_2, less than 0·7 per cent. Al_2O_3, and less than 0·15 per cent. Fe_2O_3. Sand from Fontainebleau in France contains only 0·01 per cent. Fe.

In the provinces of Areto and Grosseto (Italy) there are good siliceous sands for glass, the percentages of silica being higher than with the French sands.

[3] The German law of 1895 forbids glass-works from allowing gases containing more than 0·01 per cent. by volume of SO_2 to escape from their chimneys, and this renders the use of sulphate difficult. In any case it is necessary to pass the chimney gases through cylinders or towers filled with lumps of limestone kept moist with a spray of water. A solution of calcium sulphite and bisulphite is thus obtained which can be utilised in various industries, while CO_2 escapes.

The replacement of sodium sulphate by the carbonate has been prophesied by many now that the price of the latter is so low:



$$2Na_2SO_4 + 6SiO_2 + C = 2\begin{array}{l} \quad ONa \\ Si{=}O \\ \quad >O \\ Si{=}O \\ \quad >O \\ Si{=}O \\ \quad ONa \end{array} + 2SO_2 + CO_2 \text{[1]}$$

Sodium chloride or fluoride cannot be employed because it is too volatile and is not decomposed by SiO_2 except in presence of air and of steam, with loss of chlorine, HCl, and HF. For ordinary potash glass, wood ashes are employed, and for the best glasses pure potassium carbonate. Potassium sulphate is not employed because it is too difficult to decompose.[2]

(3) **Lime.** This is used in the form of carbonate; for glass of high quality, marble s employed. In Bohemia wollastonite or calcium silicate is used, while slaked lime is rarely employed. The limestone should be as free from iron as possible and 20 parts are often used per 100 parts of silica. In order to facilitate fusion, a little calcium fluoride is sometimes added.

(4) **Lead Oxide.** This is used in the form of minium, Pb_3O_4, which is then converted into lead peroxide, and should not contain copper or tin; besides increasing the refraction and the density, it acts as an oxidiser and purifies the molten glass.

(5) **Certain Natural Silicates.** Felspar, pumice, basalt, lava, etc., are of similar composition to glass, and may be used in glass manufacture with the addition of a few other ingredients.

(6) **Broken Glass.** The mixture of materials for the production of common glass is made with about one-third of broken glass which is present in the works or is acquired.

(7) **Decolorising Materials.** These act in two ways: by oxidising the impurities which colour the glass or by producing complementary colours which destroy the colours due to the impurities. Manganese dioxide, which has been used for this purpose since ancient times, partly acts by oxidising the green ferrous oxide, producing a yellow oxide which has a less intense colour, and partly forms manganic silicate which is violet and eliminates the greenish-yellow colour, forming colourless manganous silicate. Nickel oxide is sometimes used instead of manganese dioxide. As oxidising agent to remove the yellowish tint due to sulphides and sulphur, use is now generally made of sodium nitrate (up to 1 per cent.).

Arsenious oxide is also used, and the addition of a little antimony sulphide or oxide increases the lustre of the glass.

(8) **Various Constituents.** Glasses containing barium oxide are more pasty in the fused

---

[1] The reaction may be explained by assuming that the sodium sulphate dissociates at a high temperature: $Na_2SO_4 \rightleftarrows SO_3 + Na_2O$, but this reaction is reversible and the equilibrium is disturbed and the Na_2O so fixed more easily by the silica owing to the presence of the carbon, which withdraws oxygen: $2SO_3 + C = 2SO_2 + CO_2$; decomposition of a further quantity of the sulphate then follows and so on. If excess of carbon were present, CO would be formed: $SO_3 + C = SO_2 + CO$ and sulphide would then arise (*see* p. 627). This explanation is perhaps more acceptable than that assuming the more or less complete decomposition of the sulphate into sodium sulphite or sulphide.

[2] The reaction between soda and silica begins at 700°, increases at 800°, and is complete at 950°. The soda melts at 850° and a glass is first obtained with the proportions $Na_2O + SiO_2$, this melting at 1150°. When a mixture of $Na_2CO_3 + 10SiO_2$ is fused, at 1150° part yields the silicate, Na_2O, $4SiO_2$ (corresponding with soluble glass) and part an insoluble silicate richer in silica. The reaction between soda and alumina in the ratio $Na_2O + Al_2O_3$ occurs at 1150° with formation of a soluble aluminate, which at a higher temperature dissociates, a little soda evaporating; if, however, $10SiO_2$ is present, no soda evaporates even at 1350°. If various quantities of lime are added, ordinary glasses are obtained, the resistance of these towards acids increasing with the quantity of silica combined.

A mixture of sodium sulphate and silica in the proportion, $Na_2O : 4SiO_2$, begins to react at 925° and the reaction is complete at 1310° in forty-five minutes; if the proportions are Na_2O and $2SiO_2$, the reaction does not go beyond 50 per cent. even if the temperature is kept at 1370° for two hours or at 1400° for one hour. Addition of calcium sulphate to a molten glass results in the formation of calcium silicate and Na_2SO_4, the latter reacting further on addition of fresh silica to give sodium silicate.

state and serve well for moulded articles. Zinc oxide increases the mechanical and chemical resistance and the refraction, and diminishes the dispersion (optical glass). Magnesium oxide in the proportion of not more than 2 to 4 per cent. may be useful. Alumina diminishes the fusibility and the tendency to devitrification and increases the chemical resistance (it is added as felspar, basalt, or granite, but not as anhydrous oxide). Boric acid up to 20 per cent. raises the refractive index, the chemical resistance (with 10 per cent. B_2O_3), the hardness and the fusibility, but lowers the coefficient of expansion.

According to Ger. Pat. 217,422 of 1907, colourless optical glass is obtained by melting with an electric induction current instead of in the ordinary fire or gas furnace.

Hardened Glasses which resist fluctuations of temperature from 200° to 100°, etc., are obtained by adding MgO and ZnO to a lead glass prepared from 75 parts of sand, 13 parts of sodium carbonate, 9 parts of manganese carbonate, 6 parts of zinc oxide, and 50 parts of minium; the coefficient of dilatation is not high and it may be used for lamp glasses (*Cristalleries de Baccarat*). In Germany the same and even better results were obtained at an earlier date with borosilicate glass, which is the best for the manufacture of steam gauges for high pressures (*see above*, Thermometer Glass).

GLASS MANUFACTURE. The materials, which have been previously analysed, are finely powdered and mixed in the proportions required for the desired quality of glass.[1]

These substances are melted in suitable fireclay pots placed in melting furnaces constructed of highly refractory materials.[2]

---

[1] Here are, for example, two recipes for window or bottle glass:

	Sand	Na_2SO_4	Soda	$CaCO_3$	Coke	Potassium Nitrate	MnO_2	As_2O_3	Sb_2S_3
I. kilos	100	37	5	36	2	—	—	—	—
II. ,,	100	—	39	17	—	2·8	0·400	0·280	0·140

In these recipes the 5 to 6 per cent. of alkali which is lost during treatment is already allowed for. In Italy soda glasses are often obtained with the following mixture: sand, 38·5 per cent.; calcium carbonate, 7·74; sodium carbonate, 15·5; sodium nitrate, 1·5; broken glass, 36·5; arsenious acid and manganese dioxide, 0·25.

[2] The gas furnaces of Fr. Siemens are now general in the glass industry, and consist of three perfectly distinct portions, the generator or producer, the true melting furnace, and the regenerator. Siemens' gas producer (1861), which has enabled 30 to 40 per cent. of fuel to be saved, is based on the principle of passing a current of air or steam through the red-hot fuel, consisting of peat, wood residues, or preferably coke, arranged on an inclined plane, *B*, the lower part of which consists of a grate arranged in steps, *C* (Fig. 246); the whole is enclosed in a brickwork chamber. Energetic combustion is started only in the lower portion of the heaped-up fuel, through which air is drawn from within; at the same time a fine spray of water is introduced through the tube, *E*. The products of combustion pass through the remaining fuel producing a kind of distillation with formation of a gas of high calorific power, whilst the CO_2 is reduced to CO and the steam is decomposed by the red-hot carbon into oxygen and hydrogen. The mean composition of such producer gas (p. 489) is 28 to 33 per cent. CO, 1½ to 4 per cent. H, 0·8 to 4 per cent. CO_2, 62 to 64 per cent. N, with a calorific power of 800 to 1000 cals. per cubic metre.

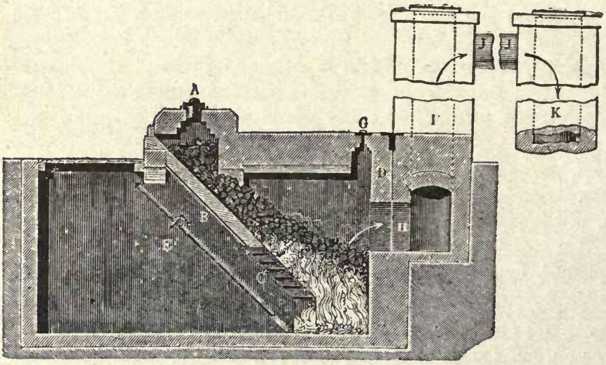


Fig. 246.

The hot gases from the producer pass along a flue, *I*, about 4 metres high, through a large, wide, horizontal iron tube, and then when somewhat cool descend a vertical flue, *K*, at the bottom of which is a cistern of water where the tarry products of the distillation of the fuel condense; these would otherwise obstruct the succeeding pipes. The gas in *I* is hot, whilst in *K* it is cooler, so that there is a pull from *I* towards *K*, and this causes a strong air draught through the grate of the producer without any necessity for fans or air injectors.

The gases from *K* pass through small hot flues, *a* (Fig. 247) or *k'* (Fig. 248), situated below the melting furnace, into a common chamber, *A*, whence they pass through a reversible valve, *E*, for half an hour into the chamber, *C*, whence they are carried through the flue, *C'*, into a couple

Apart from Siemens' furnaces, similar types evolved by Nehse and Dralle are now employed, and it is estimated that to-day, for completely working 100 kilos of glass,

---

of red-hot regenerators described below (Figs. 248 and 249). Meanwhile the gases from the melting furnace, *f′* (Fig. 248), pass through the flue, *B′*, into the chamber, *B*, after having given up their heat to the other pair of regenerators, *d′* (Fig. 248), and then pass to the chimney through the flue, *D*. After half an hour *D′* has cooled somewhat, whilst *d′* has become red hot. The current of gas is then reversed by altering the position of the reversible valve, so that the gases from the generator first pass through *B* and *B′* and then into the red-hot regenerator, *d′*, whilst the gases from the melting furnace then heat the colder regenerator, *D′*, to redness and pass through the flue, *C′*, into the chamber, *C*, and thus to the chimney through *D*.

Since this valve does not close perfectly, it has been replaced by a valve similar to the Glegg valve used in gas-works (*see* Lighting Gas, Vol. II., " Organic Chemistry ").

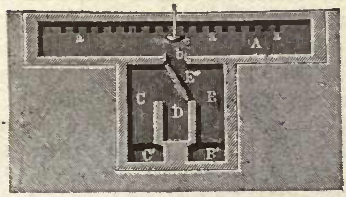


FIG. 247.

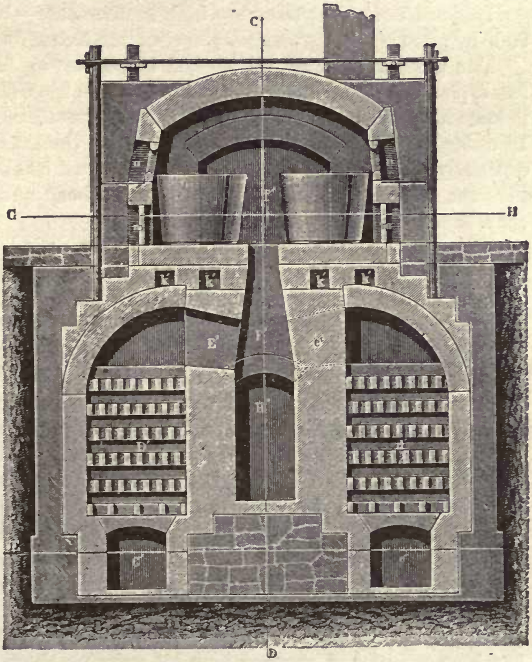


FIG. 248.

The regenerators (Fig. 249) are arranged in two pairs under the melting furnace, and consist of two systems of vertical chambers filled with firebricks which are arranged at equal intervals so that plenty of space is left for the passage of the gas. A pair of regenerators heated to redness

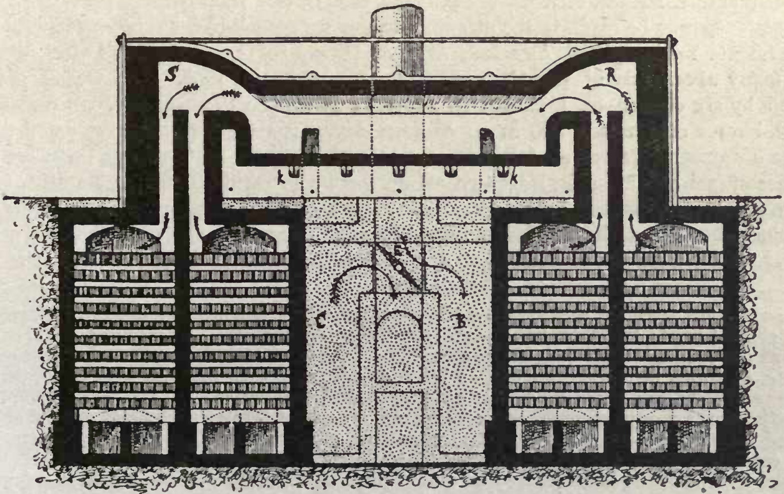


FIG. 249.

and comprising the two halves, *D′* (Fig. 249), serve to heat, on the one hand (*D′*), the gas from the producer, and, on the other hand, the air which passes to the melting furnace. The hot gases and air pass through separate flues into the common chamber, *E′*, and then pass to the

130 kilos of coal are required. The heat is still incompletely utilised, but three to four times less fuel is used than in the old furnaces. At the surface of the molten glass impurities and the excess of alkali sulphates and chlorides (glass-gall) separate and are removed with an iron ladle, or if present in small quantities are allowed to volatilise. The clarified glass is then ready to be worked.

It is not worked at this very high temperature—1000° to 1100°—but is cooled to about 800° by allowing cold gases (air) to circulate in the flues, k', under the furnace floor.

The pasty glass may be worked in all ways: blown, drawn into slender threads or fused piece to piece, but if kept too long at a high temperature or remelted several times, it loses its transparency and may become crystalline, opaque or even milky like porcelain. In order that articles made from fused glass (blown or moulded) may not be too brittle—especially on change of temperature—they must be allowed to cool slowly; for this purpose they are reheated in furnaces at a lower heat and are then cooled down in successive chambers at lower and lower temperatures.

When glass articles still pasty are rapidly cooled, *e. g.*, by immersion in an oil-bath at 60° to 120° (for readily fusible glass, or at 150° to 300° for more infusible glass), the glass becomes harder and resistant to shocks and changes of temperature, besides being less dense and behaving in a special manner towards polarised light; it serves for chemical apparatus, lamp-glasses, etc.

The preparation of glass in pots is accompanied by many difficulties and a considerable expense for pots, which easily wear out.[1] Moreover the work is not continuous because for half a day the glass is melted and the molten glass is then worked during another half day. For these reasons, attempts were made without success by Chance and Donzel to employ tank furnaces, but later Siemens succeeded in solving this problem very completely and advantageously by using the hearth of the furnace itself as a tank, and in Fig. 249 a section of one of these furnaces is shown together with the course of the gases which enter at *R* and escape at *S*, giving off their heat to the regenerators placed below.

Since the arches of these furnaces wear out rapidly (ten to fourteen months), it has been proposed to use suspended arches with an iron casing, the blocks being independent and interchangeable. To preserve the walls and the bottom from rapid wear the idea has been mooted of cooling them by covering them externally with water tubes, so that the walls and base are coated with a layer of almost solid glass which protects them from further corrosion.

There are other systems of regenerative (but not recuperative) furnaces which it would take too long to describe, and it is also impossible to describe the working of glass in order to obtain sheets, bottles, mirrors, vases, tubes, etc., in this volume.[2]

Reference may be made to the attempts to replace mouth-blowing by machine-blowing. Experiments made by the American firm of Owens in the machine-blowing of bottles cost many thousands of pounds and attained success in 1905. The Owens machine, tended by six operatives, produces as many as 20,000 bottles per day, whereas a good mouth-blower only makes 300 in an average day. The Owens patent was sold in 1907 to the European Syndicate of Bottlemakers for £600,000. In Germany there are about two dozen such machines, in Italy two, and in the whole world (in 1912) a hundred, capable of turning out four million bottles per day. They are complicated, very costly and delicate machines, but wonderful in their action, although it is not easy with them to produce bottles with a highly re-entrant base, and as it is not possible to rotate the bottle in the

---

furnace through its floor, and between the crucibles, where the mixture catches fire, producing so much heat (up to 1200°) that the mixture in the crucibles melts. These hot gases then escape through the opening in the floor at the other side of the furnace and heat the other pair of regenerators, d', which are used after half an hour for heating the air and producer gas. On p. 454 we have already seen these generators applied to coke production.

[1] The works now prepare these crucibles from a paste of fireclay with finely ground chamotte treated with a little water and minimal quantities of soda, which are carefully determined in each case. By prolonged mixing a very plastic (colloidal) mass is thus obtained (E. Weber's process, 1905), so that crucibles may be obtained which set in the gypsum mould in a few hours, and may be removed from it in two days. They should, however, rest (mature) for some months (three to twelve) in chambers kept at 25° to 30° and before using in the furnaces should be gradually heated almost to redness.

[2] *Blown window glass* is made by preparing large tubes or cylinders which are cut, opened out and stretched over a plane surface. Very thick sheets for mirrors and for covering roofs or pavements are made from cast glass.

mould during blowing, as is done in mouth-blowing, the surface of the glass is less regular and shiny, but the thickness of the walls is more regular and the mouth more perfect.

Not less wonderful are the machine of the American firm August Kadow of Toledo for making incandescent electric lamp globes (23,000 per day) and that constructed by the American Empire Machine Company for producing window panes by the automatic blowing of cylinders 10 metres long and 60 cm. in diameter for ordinary sheets. The experiments alone cost about £480,000. Such machines are common especially in America, but in 1914 one was started in Rome.

STATISTICS. The glass industry has to-day acquired a certain importance in Italy, and the supply, even of cheaper articles, is commencing to be almost independent of other countries. In 1903 about 10,000 operatives were employed in Italy in various glass-works, the output being as follows (in tons):

	1903	1910	1913
Various objects of crystal glass	46,167	70,515 (£671,000)	About 110,000 tons, of the value £1,400,000.
Sheets and bell-jars . .	17,100	19,650 (£291,050)	
Artistic glasses and enamels .	143	1,943 (£156,000)	
Beads	5,300	4,500 (£153,000)	

In 1913 the Italian glass industry consumed about 210,000 tons of coal, all imported, so that the industry carries a burden heavier than that of the forest industry and moreover such burden is aggravated by the scarcity in Italy of pure quartzose sands, so that these have to be imported. The fuel difficulty could, however, be alleviated if the coal were well utilised and losses in all phases of the working avoided.

The large Belgian glass-works, although paying a tax of 24*s.* per ton, send large quantities of glass to Germany (5000 tons in 1890 and a good part of the 18,000 tons, of the value £800,000, imported into Germany in 1908). In 1908 Belgium produced 26,000,000 sq. metres of window panes.

The Belgian glass industry employed 10,124 workpeople in 1880, about 23,000 in 1900 and about 31,000 in 1906, in 72 works. In the five years 1891 to 1895 Belgium's average exports were of the value of £1,920,000, and in the five years 1901 to 1905 the mean annual exports were of the value of £3,440,000, of which 50 per cent. was consumed by Britain and British possessions (India, Australia, and Canada); 50 per cent. of the Belgian exports consist of window glass, and 30 per cent. of mirror glass.

In Germany in 1903, 61,000 workpeople were employed in the glass industry, and 156,000 tons of glass were exported, of which 100,000 tons consisted of green bottles, of the value of £1,400,000, and 56,000 tons of other articles. On the other hand, Germany imported 15,000 tons of glass, of the value of £520,000. In 1908, 15,000,000 sq. metres of ordinary glass sheets were made in Germany.

In 1908 Germany imported 18,275 tons of varied glass for mirrors and tableware and in rods, tubes, etc., the value being £735,000; the exports were 177,289 tons in 1907 and 155,683 tons, of the value £5,200,000, in 1908.

Austria also exports much glass (47,000 tons in 1887; in 1913 Italy alone imported about 4000 tons of glass from Austria).

In France the glass industry occupied 37,000 workpeople in 1896 and about 43,000 in 1901, of whom 800 were employed in the manufacture of optical glass, 10,900 in the manufacture of bottles (14,700 in 1906) and 3600 in the manufacture of window glass (with production of 6,000,000 sq. metres of glass sheets). In 1897 the imports amounted to 24,000 tons, of the value of £600,000, and the exports to 104,000 tons, of the value of £1,080,000. In 1906 the imports rose to 30,000 tons, of the value of £720,000, and the exports to 132,800 tons, of the value of about £1,680,000.

France imported the following quantities of sand for glass-making: 27,767 tons in 1913, 16,400 in 1914, 10 in 1915, and 27 in 1916.

In the United States three Pittsburg works alone have a total capital of £2,480,000, and employ 5000 workpeople. The annual wages of these amount to £600,000, and the production is 466,000 tons. The Rochester Tumbler Company is the most important glass and bottle factory in the world. It produces 1,000,000 articles per week, and covers a surface of six hectares.

Forty per cent. of all the glass manufactured in the United States comes from Pittsburg. The Macbeth Emaux Glass Company is the largest lamp-glass works in the world. In 1905 there were 400 glass-works in the whole of the United States with an invested capital of £18,000,000, employing 64,000 workpeople, paying £7,600,000 yearly in wages, consuming prime materials of the value of £5,200,000, and manufacturing finished products of the value of £16,000,000, including £6,600,000 of various bottles, £4,400,000 of pressed and blown glass, £2,320,000 of window glass, and £1,600,000 of plate glass. In 1909 there were 363 glass makers with a capital of £25,800,000.

The United States supply half the world's production of flint glass plates, as is shown by the following summary for 1905: France, 1,420,000 sq. metres; Belgium, 2,350,000 sq. metres; Germany, 1,410,000 sq. metres; Holland, 80,000 sq. metres; Italy, 80,000 sq. metres; Austria-Hungary, 275,000 sq. metres; Russia, 310,000 sq. metres; England, 739,000 sq. metres; United States, 5,500,000 sq. metres.

England imported glass and porcelain to the value of £3,817,000 in 1910 and £4,040,000 in 1911; the exports being of the value £4,352,000 in 1910 and £4,714,000 in 1911.

In 1908 Russia produced 8,000,000 sq. metres of sheet glass.

CALCIUM CARBIDE : CaC_2

This product has acquired importance only during recent years, but was obtained by Wöhler in 1862 by heating an alloy of calcium and zinc with carbon. It was obtained in the electric furnace after many attempts by Borchers in 1891, and the first patent was taken by Böhm in the same year. In 1892 it was also obtained accidentally by Wilson, and was then at once prepared in the electric furnace by Moissan, from which time the process became industrial.

When chemically pure, it forms transparent crystals of sp. gr. 2·22, and is obtained by heating calcium oxide, prepared by heating pure marble to redness, with pure carbon (sugar charcoal), the reaction being endothermic: $CaO + 3C = CO + CaC_2 - 105,350$ cals. C. A. Hansen (1909) and Rothmund showed that during this reaction an equilibrium is established by the pressure of the CO and that the reaction starts at 1275°, and only continues at 1450° on condition that the partial pressure (*see* p. 74) of the CO is kept below the critical limit; otherwise the reaction ceases.

Calcium carbide is very inactive towards most reagents and insoluble in all solvents, but immediately decomposes in contact with water and with acids with production of acetylene gas, $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. It is therefore necessary to keep it always in well-closed bottles and thus avoid access of moisture.

At high temperatures it is an energetic reducer of metallic oxides and of the dry chlorides, a carbide of the new metal being formed or the metal itself separated from the corresponding oxide. When CO is passed over the carbide at 250°, carbon (lamp-black) separates. The quantitative fixation of nitrogen by the red-hot carbide was described in the chapter on Calcium Cyanamide (p. 368). Calcium carbide, especially when fused, is a good electrical conductor.

When heated in a sealed tube at 800° to 1000°, calcium carbide dissociates at 800° to 1000° into its components, C + Ca (Moissan, Le Chatelier, 1913), and even in a vacuum at 800° to 1500° the carbide loses in value.

As the carbide is formed by a thermal and not an electric process, the arc being used for the purpose of attaining the high temperature required, either alternating or continuous current furnaces may be employed.

Erlwein and Engelhardt (Ger. Pat. 206,175 of 1907) have proposed the use of induction furnaces in which there is less loss of thermal energy, but these are uneconomical and have not been a success in practice.

Formerly use was made of block electric furnaces, which worked discontinuously and were of small capacity (200 to 300 h.p.), but the size has been gradually increased, until now furnaces taking 1500 ampères at 60 to 100 volts are employed.

We shall describe only a single type of furnace, that of Tenner; this is lined internally with refractory material and has a movable bottom which acts as the negative electrode and is formed of a car which carries an iron plate covered to a depth of 20 cm. with a compact layer of coke held together by tar. The positive electrode of carbon may be lowered from the top of the furnace. The gases which are formed during the reaction, consisting of carbon monoxide at 2500°, escape through a flue. When the furnace is ready, connection is established between the poles of a dynamo, the anode being then lowered until an electric arc is produced; the finely powdered mixture of 56 parts of calcium oxide and 36 parts of coal is then charged in through a small opening so that it covers the anode at the bottom of the furnace to a depth of 30 cm.[1] The mass then becomes heated up to 3000° or higher. Further materials are added during several hours and then, after the molten or crystalline calcium carbide has cooled, it is discharged by removing the car through a door; another car is then introduced and the operation recommenced. The solidified block of carbide, weighing 300 to 400 kilos, is dropped on to an iron grid, the surface layer of mixture which has not completely reacted being scraped off and the

---

[1] In the early years of this industry it was regarded as indispensable to charge the electric furnaces with finely-powdered materials, and a considerable amount of energy was consumed in the disintegration, besides which the CO evolved encountered marked resistance, and sometimes caused projections of material from the furnace with danger to the operatives and alteration of the composition of the reacting mass; thus, a continuous, tedious and dangerous mixing of the mass was necessary to facilitate the emission of the CO. Since the reaction takes place by fusion of the lime and dissolution in this of the carbon to form fused calcium carbide, in which further quantities of lime and coal dissolve, it will be understood that, even if the reacting materials are used in pieces like nuts, the final product is equally homogeneous, and the inconveniences referred to are avoided.

Prime Materials. The lime or limestone and coal should be of a certain degree of purity. The limestone should not powder on calcination, and should contain more than 95 per cent. of $CaCO_3$, and less than 1 per cent. of magnesia, as this does not give carbide and renders the lime less fusible, so that the reaction then requires a higher temperature, with an increased consumption of electric energy and greater difficulty in the discharge of the fused carbide. Alumina leads to similar inconveniences; with only traces of magnesia and alumina, the presence of silica (up to 5 per cent.) is not harmful, as either it is reduced to silicon and this vaporised, or with the iron it forms ferro-silicon which separates at the bottom. Sulphates in small proportion in the limestone are not injurious on condition that alumina is not present, since the calcium sulphide formed with the carbide does not give hydrogen sulphide with water, whereas aluminium sulphide does give H_2S, and this on burning yields SO_2, which attacks the burners and contaminates the air. The limestone is, however, unusable if it contains more than 0·006 per cent. of phosphorus (as phosphate), as this gives calcium phosphide, which with water produces hydrogen phosphide; the latter introduces the danger of spontaneous ignition of the acetylene, and when burnt yields the injurious phosphoric anhydride. Good acetylene should contain less than 0·04 per cent. (preferably only 0·002 per cent.) by volume of hydrogen phosphide.

The carbon (wood charcoal, anthracite or coke) which is most economical and is most commonly used is coke, in spite of its electrical conductivity and its high ash content (this should, however, not exceed 8 to 9 per cent. so as not to lower the yield too much). Wood charcoal is better as it does not conduct the current so well, is more porous, and so allows of the ready escape of the gases formed in the reaction, and contains little ash, and so permits the use of a less pure limestone (with even less than 95 per cent. of $CaCO_3$), which could not be used with coke. Anthracite is very compact, but may be used in large electric furnaces, as it contains little ash (about 4 to 5 per cent.). If the carbon contains a little phosphorus (up to 0·01 per cent.) it may be used, as this vaporises in the furnace. Very dry coal must always be employed.

The electrodes are important, especially as regards the economical working of the furnaces. They may be made of graphite or amorphous carbon; the latter lend themselves to use in large modern furnaces, whereas in block furnaces graphite electrodes were almost indispensable, although their high consumption (up to 90 kilos per ton of carbide) constituted a serious expense, and the American furnaces could not use electrodes of artificial Acheson graphite (*see* pp. 438 and 440) owing to its cost. In modern furnaces the consumption was diminished to 20 kilos (before the European War the electrodes cost about £14 per ton). Soft and hard electrodes are made; the former are the less brittle, but are used up the more easily by the air during their action.

With a current density of 8 to 10 ampères per sq. cm. of section the electrodes are heated to redness, so that in practice this current should not be exceeded, and as the temperature in the active zone of the furnace is proportional to this density, the required temperature of 2400° to 3000° necessitates a current of 1 to 2 amps. per sq. cm., this being obtained only with a voltage of 30 to 35 volts. Further, to maintain a given temperature in the carbide furnace the current density must be increased as the voltage rises and vice versa. Small furnaces work better with low voltages (30 to 40), but with large furnaces regular working has been attained with 90 volts. In small furnaces use was once made of carbon electrodes of 10 cm. side for currents of 500 ampères, but nowadays electrodes of 60 cm. side are made (by uniting many small electrodes into compact blocks) for 25,000 to 30,000 amps. Such electrodes, inclusive of the connections, weigh as much as 10,000 kilos.

residual ingot passed to the disintegrators, and then packed in metal boxes. With block furnaces using powdered lime-carbon mixture, the losses of material are high, and to obtain 1000 kilos of carbide sometimes more than 3000 kilos of the mixture are used, whereas only 1500 are now required with modern continuous fusion furnaces. Further, the consumption of electrodes has fallen from 100 to not more than 20 kilos per ton of carbide, and the cost of labour from £1 16*s.* to 16*s.* (*see* Ger. Pats. 194,880 and 195,189, 1906).

In fusion furnaces continuous discharge is obtained if a very high temperature is maintained throughout the reacting mass, *i. e.*, when powerful transformers are available. It became necessary, however, to find a practical method of tapping the fused carbide gradually as a certain quantity forms, and this was attained by using the arc to melt the crust of the solidified carbide at the point where it was wished to run it off; in this way orifices 15 to 20 cms. in diameter were made; these permit of the discharge of even the pasty mass, and are not easily obstructed by solid slag or crust suspended in the fused carbide. This electrical discharge is naturally costly, as it requires supplementary electrodes 10 to 20 cm. in diameter, with a current of 2000 to 4000 amps at 50 to 60 volts, and a consumption of 150 to 300 h.p., 1 to 2 kilos of electrodes being used per ton of carbide produced. Helfenstein uses closed electrical furnaces so as to utilise the large quantities of pure carbon monoxide evolved; such furnaces (Ger. Pats. 224,878, 226,956, 229,302, and 235,061 of 1909 and 1910) use 6000 or even 10,000 h.p. Another form of modern furnace, not closed for the collection of the CO, is shown in Fig. 250; the electrodes *A*, mounted on the car, *C*, are able to perforate a crust 50 cm. thick in twenty minutes. The furnace is composed of a firebrick skeleton lined with carbon; the 4000 to 6000 kilowatt transformers, *T*, are cooled by the fan, *V*, and the electrodes *E*, suspended from *P* and receiving current from the leads, *k*, may be lowered into the furnace, *F*, by means of a pulley worked either by hand or by the motor, *W*. Furnaces are constructed of 18,000 kilowatt size, capable of turning out 100 tons of carbide per day. The Terni works in Italy and certain others in France and Canada use Tofani furnaces, these consuming 3000 h.p. (triphase current).

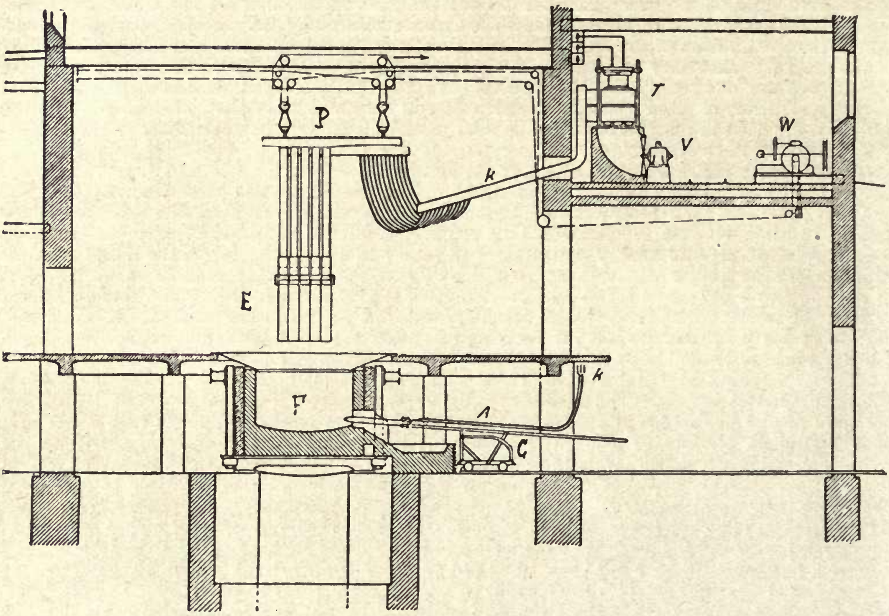


FIG. 250.

The theoretical consumption of energy is 24 h.p.-hours (*i. e.*, 17·66 kilowatt-hours) for 8 kilos of carbide, and in practice this amount of energy (1 h.p.-day of twenty-four hours) yields 3·5 kilos of carbide in small block furnaces, 4·2 in small discharge furnaces, 5·6 kilos in 4000 h.p. furnaces, and 6 kilos in 6000 h.p. furnaces. With large furnaces an average output of 1500 kilos per h.p.-year may be assumed—for a good carbide yielding 305 litres of acetylene (at 15° and 760 mm.) per kilo.

The approximate cost price of 1 ton of carbide may be calculated as follows (large furnaces):—

	Open Furnaces	Closed furnaces with recovery of the CO
	s.	s.
Anthracite: 670 kilos at 36s. per ton .	24·1	24·1
Lime: 1030 (or 950) kilos at 20s. per ton.	20·6	19·0
Electrodes: 33 (or 20) kilos at £14 per ton	9·2	5·6
Packing	25·6	25·6
Electrical energy: 170 kilowatt-days (158 for closed furnaces) at £2 per h.p.-year	26·4	24·5
Wages and salaries	15·2	8·8
Grinding of raw material, carbide, etc. .	8·0	2·4
General expenses, sinking fund, etc. .	12·0	10·4
Cost of 1 ton of carbide packed, in works	141·1s.	120·4s.

The practical application of carbide for lighting purposes is known to all, and the contrivances for the preparation of acetylene vary very greatly. It is now used metallurgically for hardening steel, and as a reducing agent for various metallic oxides, salts, etc.; the metals Cu, Pb, Ag and Ni are thus easily obtained from the corresponding dry chlorides mixed with a little metallic oxide: $4CuO + CuCl_2 + CaC_2 = 5Cu + CaCl_2 + 2CO_2$. It is used for the production of acetylene for the oxy-acetylene blow-pipe, for illuminating purposes, etc. (p. 191). It is also used in large quantities to-day in the manufacture of calcium cyanamide (*see* p. 368), from which during the European War enormous quantities of ammonia were prepared for the manufacture of nitric acid or ammonium nitrate.

Considerable amounts of acetylene are now used to obtain by the Machtolf process very fine smoke-black and very pure hydrogen for aeronautical uses. The gas is used also for the preparation of the various chloro-derivatives of acetylene, which are excellent non-inflammable solvents used in place of benzine (*see* "Organic Chemistry"). The manufacture of alcohol and of acetic acid from acetylene has also been attempted.

STATISTICS. This industry, which has rapidly acquired very large proportions and extended to almost every country, has been able to continue and overcome competition only in those places where electrical energy is cheap. Italy is amongst those nations which are most favoured in this respect, as it has cheap water-power, but the industry is helped more especially by the protective tariff of £4 per ton which allows Italian manufacturers to sell carbide at low prices abroad and at high prices in Italy.

The Italian production, imports, and exports are given by the following figures:—

	Production tons	Price per ton s.	Exports tons	Imports tons
1900	2,800	—	—	—
1903	16,250	—	5,000	—
1905	28,200	176–200	8,955	688
1908	35,750	192–224	4,840	1760
1910	36,515	—	2,172	2708
1911	32,750	—	8,399	70
1912	37,293	—	10,428	19
1913	49,118	208–296	11,037	80
1914	46,118	224–232	6,042	11
1915	49,189	264–272	5,132	3·5
1916	—	—	4,215	61
1917	—	—	38	6

The world's production of calcium carbide in 1909 was estimated at about 280,000 tons, a part—always increasing—being used for the manufacture of calcium cyanamide. In 1912 the direct consumption of carbide in the world was 250,000 tons.

In September 1910 a world's trust was formed embracing fifty-seven carbide factories in seven countries, these producing 150,000 tons, but having a capacity of at least 225,000 tons. The first result of the formation of this syndicate was a considerable increase in the price of carbide in all countries, whereas in 1909 prices had fallen owing to excessive production and insufficient use of carbide in the calcium cyanamide factories, which still struggled with technical difficulties. The output afterwards became more and more regular, and for 1911 is shown, together with consumption, in the following table[1] (in tons)—

	Production	Consumption
Norway and Sweden	52,000	4,000
United States .	50,000	37,000
France . . .	32,000	31,500
Italy . . .	32,000	24,000
Switzerland . .	30,000	4,000
Austria and Hungary	22,500	17,000
Spain . .	18,000	16,000
Canada . .	12,000	8,000
Germany . .	7,000	36,000
England . .	2,000	16,000
Other countries .	5,200	63,800
Total .	262,700	257,300

During the European War the output of carbide in all countries increased enormously owing especially to the great demands of the metallurgical industry (autogenous welding and cutting of metals), and to the amounts required for making ammonia (from calcium cyanamide) for conversion into ammonium nitrate and nitric acid. It appears that in 1916 Germany produced 600,000 tons of calcium carbide for the manufacture of calcium cyanamide alone.

To protect lump calcium carbide from moisture it has been proposed to coat it with graphite (Ger. Pat. 254,305), or to treat it with nitrogen in the hot so as to form a superficial layer of calcium cyanamide (Italian Carbide Company, Ger. Pat. 257,891, 1912), or to heat it strongly in presence of CO and CO_2, so as to form on it a deposit of carbon (Morani, Fr. Pat. 448,077).

Commercial carbide forms greyish-yellow lumps the size of peas or walnuts, and should not contain more than 10 per cent. of dust; it has a crystalline fracture. Its value depends on the yield of acetylene; the chemically pure product gives theoretically 348·8 litres of the gas (at 0° and 760 mm.) per kilo, but a good commercial product yields 300 litres and inferior qualities giving less than 280 litres are common.

Before the European War carbide cost £12 to £14 per ton in Italy, but during the war the price rose to as much as £100.

[1] In *France* carbide costs £3 12*s.* more per ton than in Sweden, but in 1908 it enjoyed a protective tariff of £2 8*s.* per ton. There are 10 amalgamated works in France capable of producing 40,000 h.p. and 2 independent works commanding 8000 h.p. In 1904 only 18,000 tons of carbide were produced on account of the diminished demand, whilst the ordinary production is about 30,000 tons. The imports were 2162 tons, and the exports 5058 tons in 1911. Until 1912 French works using the Bullier furnace paid 16*s.* per ton for patent rights.

In *Germany* the carbide industry consumes about 10,000 h.p.; the production is about 8000 tons, but it is not increasing because Germany is less satisfactorily placed than other nations in regard to the cost of electrical energy, and there is no protective tariff for carbide. On the other hand, the consumption is increasing and the imports in 1904 were 14,840 tons, 17,256 tons in 1905, 22,727 tons in 1906, 25,834 tons in 1907, 29,000 tons in 1908, 27,000 tons in 1909; in 1911 the consumption was 36,230 tons, and in 1913 the imports were 46,725 tons. Of the imports into Germany about one-third come from Norway, about one-half from Switzerland, and about one-sixth from Austria. In 1913 the German consumption was 55,000 tons; 30,500 tons for lighting, 17,000 tons for the autogenous welding of metals, 7000 tons for making calcium cyanamide, and 500 tons for other purposes. The consumption for lighting purposes is estimated to be distributed thus: for miners', cycle and automobile lamps, 15,000 tons; for fixed plants, 11,000 tons; for central stations, 4000 tons; for acetylene dissolved in acetone, 200 tons, and for torches, etc., 300 tons.

Switzerland uses about 66,000 h.p. in its carbide works.

Prior to 1908 Japan had only one small works which supplied the consumption of 90 tons per annum, but in 1909 a 10,000 h.p. works was erected.

The various factories in Austria (the most important are those of Sebenico and Almissa in Dalmatia) have a capacity of about 80,000 tons per annum, but as the home consumption is only 20,000 tons, the output is limited by the International Syndicate to one-half of the capacity, and a large amount still exported. Before 1909 only 35,000 h.p. were utilised.

In 1910 England imported 12,500 tons of carbide.

In 1911 the United States exported 14,000 tons.

In 1910 Norway produced in a single factory quite 30,000 tons of carbide, and Sweden has an output one-half that of Norway.

The Argentine in 1912 consumed 12,000 tons of carbide, and has a works at Cordoba capable of producing 4400 tons per annum.

In case of dispute, a sample for analysis is taken by withdrawing 2 kilos from a single intact barrel where the parcel is less than ten barrels; otherwise 1 kilo per barrel is taken from 10 per cent. of the barrels.

Strontium and barium carbides are made in the same way as the calcium compound.

CALCIUM PHOSPHATE—CHEMICAL MANURES AND SUPERPHOSPHATES

In the section on phosphoric acid (p. 415) we have already seen how this acid may give rise to three series of salts.

TRICALCIUM PHOSPHATE, or **Tertiary Calcium Phosphate** : $Ca_3(PO_4)_2$, occurs fairly widely distributed in the soil and in rocks, forming various minerals which are described below under Phosphatic Chemical Manures. Plants absorb the phosphate from the soil and accumulate it, more especially in the seeds of cereals, vegetables, etc. The phosphates also exercise a very great influence on the development of the animal organism, as they are the fundamental constituent of bone, of which the ash (p. 404) contains up to 82 per cent. of tricalcium phosphate. This phosphate is almost completely insoluble in water and is obtained from soluble salts (alkali phosphates) by the addition of a soluble calcium salt in presence of ammonia. It separates as a gelatinous mass, which after drying forms a white amorphous powder easily soluble in acids (even in acetic acid), and is attacked by carbon dioxide dissolved in water and may thus be assimilated by plants from the soil. Ammonium citrate solution dissolves 1 per cent.

The **SECONDARY PHOSPHATE,** $CaHPO_4 + 2H_2O$, is also called **Dicalcium Phosphate,** because the calcium has replaced two atoms of hydrogen of the phosphoric acid. It is found ready-formed in small crystals in guano and is obtained as an amorphous powder by mixing a solution of disodium phosphate with calcium chloride in presence of a little acetic acid. It dissolves in a little water, but is decomposed by much water with production of a turbidity consisting of tricalcium phosphate, whilst the remaining solution acquires an acid reaction. Ammonium citrate solution dissolves 8 per cent. On heating to redness it is transformed into calcium pyrophosphate, $Ca_2P_2O_7$.

The **PRIMARY PHOSPHATE** (**Monocalcium Phosphate**) : $Ca(PO_4H_2)_2$, is obtained from the other phosphates by treating them with the calculated quantities of phosphoric, sulphuric or hydrochloric acid. When the solution is concentrated, the salt separates with $1H_2O$ in rhombic plates, but if the concentrated solution is heated, anhydrous crystals separate. At 100°, or better at 130°, it loses its water of crystallisation and is transformed into a mixture of calcium pyro- and meta-phosphates. It is soluble in much water, whilst when treated with a little water tricalcium phosphate is formed and a very acid liquid remains.

CHEMICAL FERTILISERS

In the course of this work we have become acquainted with numerous salts, chlorides, nitrates, sulphates, carbonates, ammonium salts, phosphates, etc., and as many of these have acquired great agricultural importance, and to-day form the basis of successful agriculture by maintaining or increasing the fertility of the soil, we shall devote some pages to the important industry of artificial manures. In 1840, Liebig disproved the erroneous and traditional conceptions then prevalent[1] in connection with substances which fertilise

---

[1] Until the middle of last century, and, if we wish to go backwards in history, also from the remotest antiquity when agriculture itself arose, the only substance which was supposed to supply and replace the nourishment periodically removed from the soil was stable manure and excrements in general. Guano, the excrement of birds, has been used agriculturally in Peru since 1300 (during the rule of the Incas), and the birds which produced it were protected by law.

The action of dung was attributed by Palissy in 1550 to the soluble salts which it contained.

the soil, by numerous experiments and treatises, especially by his book on agricultural chemistry and his celebrated pamphlet "Die Latrinenfrage," in which he showed that all green plants obtain their most important nourishment in the form of mineral matter, carbon dioxide, ammonia, water, phosphoric, silicic and sulphuric acids, lime, magnesia, potash (and soda), iron, etc. Human and animal excrements are important not on account of the organic matter which they contain, but on account of the inorganic substances produced from these on putrefaction, by which the organic carbon is transformed into carbon dioxide and the organic nitrogen into ammonia, nitrates, etc., so that in order to maintain the fertility of the fields it suffices to treat the soil with inorganic salts which are utilised by the plants and which are formed to a large extent during the putrefaction of organic matter, such as stable manure, etc.

The use of artificial chemical manures has extended and continuously increased only since this precise and rational theory was enunciated by Liebig.

In order to determine the absolute value of a chemical manure it is necessary to consider it apart from other agricultural factors, which are also of great importance, such as the character of the soil, the amount of heat and light, etc. Wolff, Sachs, Stohmann, and others made artificial cultures of plants in water only, in which they dissolved various mineral salts. On the other hand, Hellriegel employed quartz sand (previously boiled with acid and washed with water), to which he then added the various inorganic chemical manures which he wished to study, and watched the growth of the various plants.

The result of all these experiments was that lime, potash, magnesia, iron, phosphoric and sulphuric acids, nitrates, ammonia, and nitric acid, all in the state of salts, are indispensable to vegetation, whilst the plants absorb the carbon, oxygen, and hydrogen which are necessary to their development from the carbon dioxide of the atmosphere and from water.

Atmospheric nitrogen is not directly assimilated, as was shown by Boussingault, although we have already seen, in speaking of nitrogen, that certain micro-organisms may serve as intermediaries, as in the case of leguminosæ, by assimilating free nitrogen (p. 350).

In the case of the ordinary commonly cultivated plants, the addition to the soil of potash, phosphoric acid, and nitrogen is always indispensable, because the soil contains little of these elements, and is easily exhausted.[1] In acid and peaty soils phosphates are almost

---

In 1780, Leblanc showed the importance of ammonium salts for vegetation, and Sprengel confirmed this idea and added that mineral salts in general play a great part in vegetation. It was, however, through the influence of two agriculturists, Thaer in Germany and Dombasle in France, from 1800 to 1840, that in Europe a theory prevailed that the importance and efficacy of stable manure was due not to mineral salts, but to the organic humus which is formed during its fermentation and putrefaction.

The influence of this erroneous theory has extended to our own days, and we still find it amongst the old farmers who have not yet opened their eyes to the light of modern science.

The advantages of chemical fertilisers over stable manure may be seen when it is considered that 1000 kilos of dung contain only 5 kilos of assimilable nitrogen, 2 kilos of phosphoric acid, and 6 kilos of potash, whereas similar quantities of fertilising products may be obtained from 30 kilos of Chili saltpetre, 10 kilos of superphosphate, and 10 kilos of potassium chloride.

The theory of fertilising is now more complex than in Liebig's time, and it has now been shown that the fertility of the soil depends, besides on these salts, also partly on the presence of certain organic materials (humus), on various colloidal substances, and on the biochemical functions of numerous bacteria (*see* p. 350).

[1] The use of chemical fertilisers has enormously increased agricultural production, and thus satisfied the growing needs of the increasing population of the world. The total value of the agricultural production has reached £240,000,000 in Italy, where the total cultivated area is 26,000,000 hectares, £600,000,000 in France (area 50,000,000 hectares), and £800,000,000 in Germany (51,000,000 hectares). Calculation shows that in France the various crops remove annually from the soil about 600,000 tons of nitrogen, 300,000 of P_2O_5 and 755,000 of potash.

The amount of nitrogen extracted per annum from a hectare of soil under different crops is as follows :

Wheat	31	hectolitres	with 66	kilos of nitrogen (including the straw).
Rye	27	,,	,, 57	,, ,, ,, ,,
Barley	36	,,	,, 51	,, ,, ,, ,,
Oats	54	,,	,, 62	,, ,, ,, ,,
Potatoes	730	,,	,, 33	,, ,, ,, ,,
Beet	40 tons		,, 80	,, ,, ,, ,,

As non-artificial organic nitrogenous fertilisers not of great efficacy, use is sometimes made of powdered blood (about 16 per cent. N.), horn powder (14 per cent. N.), and hide powder 7 to 10 per cent. N.).

completely absent and there is a deficiency of calcium carbonate. It must, however, be pointed out that the soil retains soluble phosphates, potash salts and ammonia, but not nitrates; the phosphates become insoluble, the alkalies are fixed perhaps by the zeolites, and the nitrates pass through the soil with rain-water in proportion to the amount of this and to the permeability of the soil.

It has been found that superphosphates exert their maximum effect when the soil contains lime and magnesia in abundance.

In 1906 *Germany* used various artificial manures of the value of £15,000,000, of which £2,880,000 was spent on ammonium sulphate, £6,000,000 on sodium nitrate, and £1,520,000 on potassium salts (200,000 tons at £7 12*s.* per ton). The rest is accounted for by superphosphates, basic slag, guano, etc. The trade in artificial fertilisers in 1912 was calculated at £40,000,000.

In 1905 *Italy* consumed more than 500,000 tons of various artificial manures, more than two-thirds of which consisted of superphosphates, of a total value of about £1,720,000.

France annually consumes about 2,000,000 tons of various chemical manures, while exports amounted to 403,296 tons in 1913, 247,620 in 1914, and 7816 in 1915.

In 1899 *Japan* imported various chemical manures of the value of £77,600, in 1906 of £3,000,000, and in 1909 the imports rose to a value of £4,000,000: £2,240,000 for soya cake, £600,000 for ammonium sulphate, £220,000 for phosphorites, £120,000 for rape cake, £100,000 for bones, £80,000 for cottonseed cake, £70,000 for sodium nitrate, £44,000 for superphosphates, and £36,000 for dried fish.

Australia consumed 10,000 tons of chemical fertilisers in 1900, and about 100,000 tons in 1910.

We have already considered potassium and nitrogenous manures when discussing the potassium salts of Stassfurt, sodium nitrate, and the utilisation of atmospheric nitrogen (pp. 347, 529 and 575). We shall now consider the phosphatic manures.

PHOSPHATIC MANURES. Under the best conditions soils contain up to 0·3 per cent. of phosphorus pentoxide, but ordinarily less than 0·1 per cent. Various crops remove considerable quantities of this substance annually. Thus wheat removes about 46·5 kilos of tricalcium phosphate per hectare, hemp 95 kilos, trefoil 111 kilos, sugar-beet 94·5 kilos, etc.

If, therefore, a corresponding quantity of phosphoric acid is not replaced and returned to the soil, this will become sterile in a short time. This is what has happened during past centuries in Greece, Sicily, Egypt, and Spain, which once formed the so-called granary of Europe, and to-day their production is enormously diminished because the replacement in adequate amount of the phosphoric acid removed by the corn was not thought of.

Liebig proposed in 1840 to render the fertilising action of bone-meal[1] more effective by first treating it with sulphuric acid in order to obtain soluble phosphates, and in 1857 he suggested the similar treatment of mineral phosphates to convert them into superphosphates. In England about 200,000 tons of superphosphates were produced in this manner as early as 1862.

Since this time one of the largest branches of modern chemical industry has arisen and has developed with startling rapidity and caused a true revolution in agricultural methods (*see below*, Statistics).

---

[1] For more than a century the beneficial effect of phosphates on the soil had been known, and they were employed as bone-meal. In 1840 the Duke of Richmond showed practically that the fertilising value of bones is due not to the gelatine and fat, but to the calcium phosphate which they contained.

In 1841 Flaming in England made the first attempt to treat bones with acids in the manner proposed by Liebig.

In 1856 Elie de Beaumont showed the value of finely divided mineral phosphates, but the results would have been more immediate and advantageous if the mineral phosphate (tricalcium phosphate) had been suitably transformed in order to render it more soluble and more easily assimilable.

Several attempts have been made in recent years to use finely ground phosphorites as fertilisers, but without marked success. The results of experiments made by Fraps and by Thorne over a series of years in Texas were published in 1917, and show that on direct fertilisation with phosphorites about 9 per cent. of the phosphoric acid applied is assimilated by the first crop, whereas with superphosphates the proportion is about 45 per cent.

The most important source of mineral phosphates which was used in the past for the preparation of manures was *guano*.[1]

The phosphatic deposits most abundantly used to-day consist of *phosphorite* which is the prime material for the superphosphate industry. It is an amorphous tricalcium phosphate, entirely of organic origin, being perhaps formed by the fossilisation and mineralisation of ancient deposits of nitrogenous guano. Unaltered teeth of different sizes belonging to various species of animals are often found in phosphorite. The phosphorite which is used for the production of superphosphates throughout the world is furnished mainly by the United States (Florida, Tennessee, South Carolina), by Algeria and Tunis (especially from the deposits of Gafsa), and in minimal quantities by Belgium and France (*see* Statistics *below*).[2]

---

[1] **Guano** is found along the coasts of Chili and Peru, and to some extent on the southern coasts of Africa and near Assab, etc. The deposits are sometimes 50 to 60 metres deep, and consist of the excreta and skeletons of aquatic birds. It forms more or less powdery clotted brownish-yellow masses, with a strong ammoniacal odour, and contains 7 to 8 per cent. of assimilable combined nitrogen, 12 to 14 per cent. of phosphoric acid, and up to 2 per cent. of potash (Peruvian), but that from Angamos (Bolivia) shows as much as 19 per cent. of nitrogen, and 7 per cent. of phosphoric acid, and that from the Falkland Islands up to 22 per cent. of phosphates. Italian guano is formed of the excrements of bats, and a similar guano abounds in many grottoes in Spain, Hungary, Turkey, Egypt, Cuba, etc. Certain ancient guanos, now fossilised, have lost their nitrogen, and are rich in calcium phosphate (phosphatic guanos or coprolites), and are treated like phosphorites. Of importance is fish guano, consisting of the residues from the great fisheries of Alaska, Norway, Japan, etc. On the coasts of the Atlantic there are forty factories in which fish oil is obtained by the treatment of 400,000 tons of fish per annum. The residues are compressed and then ground, their content of nitrogen being 7 to 8 per cent., and that of phosphoric acid, 6 to 8 per cent.; addition to the powder of 5 per cent. of sulphuric acid and a little potassium chloride yields a complete fertiliser readily assimilable by plants.

In 1903 about 80,000 tons of Peruvian guano were imported into Europe, and Norway exported 6580 tons of fish guano in 1902. The guano deposits of some of the Peruvian islands are estimated at 9,000,000 tons, while the exports are only 60,000 tons per annum.

Imports of natural and artificial guano into different countries (tons):—

	1907	1909	1911	1913	1914	1915	1916
Germany . .	63,229	56,397	60,254	61,919	19,169 (6 months)	—	—
Belgium . .	40,126	34,641	36,484	49,541	11,099 ,,	—	—
England . .	31,780	20,647	34,672	25,958	39,915	27,149	21,991
Netherlands . .	13,126	13,333	10,122	22,313	10,168	10,183	3,803
Japan . . .	18,016	307	4,949	3,093	2,102	610	—
Australia . .	30,818	23,786	24,588	1,362	—	—	—
New Zealand .	14,715	9,704	13,372	8,933	21,057	40,153	—
United States .	29,609	38,371	36,455	19,412	25,972	10,134	13,206
Italy . . .	—	114	—	—	146	—	9
France . .	—	—	—	1,352	2,502	27	—

[2] **Mineral Phosphates** now arrive at the European ports in lumps not larger than a potato, so that they may be unloaded mechanically. The phosphates of Tunis contain 58 to 65 per cent. of tricalcium phosphate, 10 to 15 per cent. of calcium carbonate, about 2 per cent. of ferric oxide and alumina, and 3 to 4 per cent. of moisture; they form grey granular or sandy masses, and are less hard than American phosphates.

The American phosphorites most used in Europe are those from Florida, in particular: the Hard Rock variety, with 75 to 85 per cent. of tricalcium phosphate, less than 3 per cent. of oxide of iron and alumina, and 3 to 5 per cent. of calcium carbonate, forms very hard, greyish-brown somewhat rusty lumps, and before shipment is slightly roasted in heaps to diminish the moisture and organic matter. The River Pebbles variety is now little used in Europe, where preference is given to Land Pebbles, which form cream-yellow, lead-blue or brownish-grey walnut-sized lumps, and small granules with a smooth surface and porous fracture, and contain 68 to 75 per cent. of tricalcium phosphate, 3 to 6 per cent. of carbonate and less than 3 per cent. of ferric oxide and alumina; these sometimes abound in marine animal remains, such as broken teeth of the saurus and ichthyosaurus, which are yellowish or black, and have saw edges. Formerly the Brown Rock variety, with 75 to 80 per cent. of tricalcium phosphate and 3 to 6 per cent. of ferric oxide and alumina, was imported from Tennessee.

Phosphorites are shipped in bulk and are sold c.i.f. at port of destination. They are weighed and sampled on arrival, six small boxes being filled for moisture determination (three each for seller and buyer), these being closed, the labels sealed with sealing-wax, and the origin, quality, name of steamer, weight, guaranteed strength and the names of the two contracting parties shown. Samples of one or more sealed bags are taken for the estimation of the

Recently a deposit of 25,000,000 tons of phosphorite has been discovered in Tennessee, one of 30,000,000 tons in the Society Islands, and another of 15,000,000 tons in the Island of Makatea (Oceania); the last, containing 80 to 85 per cent. of phosphate, 5 per cent. of calcium carbonate, and 3 to 4 per cent. of iron and alumina, is being worked by a French company.

Phosphorite is also found together with various other minerals and soils forming deposits of *phosphatic chalk* and *sand*, containing 60 to 75 per cent. of tricalcium phosphate, of which important seams abound in England, Spain, etc. The utilisation of poorer phosphatic deposits has now been also undertaken by concentrating them, that is, by increasing their strength by means of heating in furnaces, sometimes followed by treatment with mineral or organic acids. The concentration of phosphorite is sometimes also effected by levigation with water.

Very numerous deposits of other phosphates are also found in nature distributed in smaller or larger quantities, especially phosphates of aluminium, iron, and the relatively abundant *apatite*, consisting of a calcium fluophosphate, $3Ca_3(PO_4)_2$, CaF_2.

Apart from phosphorite and guano, basic slag and unfossilised bones are also used as sources of phosphoric acid.

The bones[1] are first defatted by immersion in boiling water, or preferably by treating them with carbon disulphide, petroleum benzine, or carbon tetrachloride. The gelatine is then removed in autoclaves at a pressure of 1½ atmospheres in presence of steam, which transforms the ossein into gelatine and dissolves the latter. Bones which have been simply defatted still contain 3·5 to 4 per cent. of nitrogen; after the gelatine has been removed, they contain only 0·9 to 2 per cent., and when powdered form *bone-meal* which is an effective phosphatic manure and also contains nitrogenous matter.

These bones are then employed for the preparation of *bone superphosphate*, which contains all the phosphoric acid in a form soluble in water, because there are no substances present which cause reversion as do the alumina and iron in phosphorite. Such bone superphosphate also contains 1 per cent. of completely assimilable nitrogen. The units of nitrogen in bone superphosphate are paid for apart from those of P_2O_5, and the latter units fetch 0·5*d.* to 1*d.* more than when present in mineral superphosphates; this difference is not justified by a greater fertilising power.

---

tricalcium phosphate, these being despatched to be ground and a sample taken from the flour thus obtained. If the ferric oxide and alumina exceed 3 per cent. (but not 4 per cent.), the buyer may subtract double the excess from the proportion of tricalcium phosphate found. The phosphate content is calculated on the dry product and per English ton (1016 kilos) for American phosphates and per 1000 kilos for African phosphates. One cubic metre of phosphorite weighs from 1350 (Tennessee) to 1500 (Gafsa, Tunis) kilos, whilst superphosphate weights 25 per cent. less.

[1] Bones contain from 55 to 65 per cent. of tricalcium phosphate, from 1 to 3 per cent. of magnesium phosphate, from 2 to 9 per cent. of calcium carbonate, 0·5 per cent. CaF_2, 25 per cent. of ossein (which gives glue), 5 to 15 per cent. of fat, and 10 per cent. of water. From an ox or a horse 40 to 50 kilos of tricalcium phosphate may be obtained, from a pig or a calf from 7 to 12 kilos, from a ram from 4 to 5 kilos, and the same quantity from a man. Apart from the bones of all the animals which are slaughtered daily, large quantities have been amassed in the quaternary epoch (that of primitive man) in the caves of Gallenreuth in Franconia, of Lherm in France, and of Suffolk in England, etc., and are also formed to-day in the pampas of the Argentine through periodic hecatombs of horses and cattle. Our descendants in the distant future will find bone deposits in many cemeteries of our present large towns.

Rocky conglomerates formed of bone abound in Algeria, and of these 6000 tons were exported in 1893 and 225,000 tons in 1898.

Germany imported 5600 tons of bones from La Plata and the Levant in 1903, and 1000 tons in 1907, at a price of £4 to £4 16*s.* per ton. It also imported *crushed bone* from Calcutta, Bombay, etc., to the amount of 13,500 tons in 1903 and 8900 tons in 1907 at £4 16*s.* to £5 12*s.* per ton, and also *bone-meal* from India, South America, and Russia to the amount of 6000 to 9000 tons at £4 per ton if degelatinised and at £4 16*s.* to £5 4*s.* per ton when it still contained the gelatine. To these quantities 3450 to 4500 tons of imported *bone ash* must be added at £2 16*s.* to £3 12*s.* per ton. In 1910 the imports of ground bones were 17,800 tons, and in 1911, 12,200 tons. From S. America 5500 tons of bones were imported in 1910 and 6760 in 1911.

Defatted bone and bone-meal were exported from India in 1906 to the extent of 17,060 tons, and 9400 tons in 1909. Germany imported 1750 tons of defatted bone in 1908 and 2792 tons in 1909, and exported 2330 tons in 1909.

England imported 39,031 tons of crude and calcined bones in 1909, 44,505 in 1910, and 45,876 (£226,000) in 1911.

France imported 2628 tons of calcined bones in 1913, 618 in 1914, and only 1 ton in 1915.

Bones which have simply been defatted and powdered do not keep well because a fermentation occurs which consumes a considerable portion of the nitrogen. This difficulty is avoided by moistening them with dilute sulphuric acid.

Bone-black, which is obtained by calcining the defatted bones in closed vessels out of contact with the air, is first employed as a decolorising agent in sugar refineries, after which it contains scarcely any more nitrogen, but is often further employed for the preparation of bone superphosphate, because it contains from 65 to 75 per cent. of tricalcium phosphate.

BASIC SLAG is obtained in steel-works from the dephosphorisation of steel by the basic Thomas-Gilchrist process in presence of much lime (*see* Iron). For each ton of steel, 200 to 300 kilos of slag is obtained, which floats upon the molten steel in the converter, and is easily separated from the surface with suitable ladles, when it sets to a hard spongy mass which is powdered in ball mills. Basic slag is now also obtained in open-hearth furnaces and is equal to Thomas slag. To obtain it in a more brittle condition before powdering, it is poured into water whilst still molten.

The phosphoric acid in the slag is probably present in the form of basic tetracalcium phosphate, $Ca_4P_2O_9$, united with 1 mol. of calcium silicate, $CaSiO_3$, and contains about 80 per cent. of total phosphorus pentoxide which is soluble in ammonium citrate, so that it behaves as dicalcium phosphate. It contains also from 10 to 20 per cent. of free lime, from 4 to 30 per cent. of iron oxides ($Fe_2O_3 + FeO$), and from 2 to 20 per cent. of silica. It usually contains from 14 to 16 per cent. of P_2O_5 or from 16 to 18 per cent.; for equal strength in phosphoric acid, that is preferred which contains most SiO_2.

Basic slag is placed on the market for direct consumption in very fine powder, 80 per cent. of which passes through sieve No. 100 (French scale), and its efficiency is proportional to its degree of fineness. The fertilising power of slag of 50 per cent. fineness is 10 per cent. lower than that of 75 per cent. fineness. It varies in colour from reddish brown to dull yellow (*see* Analysis *below*).

In 1892 Europe produced about 1,000,000 tons of slag; in 1899 the production rose to 1,650,000 tons, and Italy imported about 70,000 tons in 1902.[1]

The demand for this product is so great that the unit of P_2O_5 fetches almost as high a price as the same unit in the form of superphosphate.

THEORY OF SUPERPHOSPHATE MANUFACTURE. Tricalcium phosphate, however finely divided, being insoluble in water, comes into contact or is absorbed by

---

[1] BASIC SLAG

Country	1907	1909	1911	1913	1914	1915	1916
				PRODUCTION			
Germany and Luxemburg	1,803,000	1,879,000	2,160,000	2,550,000	2,067,000	1,635,000	1,592,500 (10 months)
Austria-Hungary	78,900	69,600	85,300	50,800	39,900	60,260	—
Belgium	325,000	335,000	471,000	655,000	—	—	—
France	408,000	463,000	602,000	730,000	—	—	—
Great Britain	245,000	255,500	270,000	404,000	392,194	386,098	—
Luxemburg	—	—	—	250,000	—	—	—
Russia	—	—	—	49,000	60,500	—	—
Sweden	—	6,936	12,670	18 354	15,400	18,910	—
				IMPORTATION			
Germany	164,234	279,239	403,764	441,069	234,081 six mths.	—	—
Austria-Hungary	104,472	153,704	145,465	212,788	110,153	—	—
Belgium	77,058	97,376	117,954	144,553	76,248	—	—
Denmark	—	—	11,025	8,944	10,751	—	—
France	—	—	—	—	33,750	9,981	828
England	—	15,531	23,030	51,954	16,838	—	—
Italy	129,261	93,087	114,149	119,257	23,224	1,180	2,716
Norway	29,734	23,297	30,252	34,755	34,741	26,020	8,353
Netherlands	191,123	154,539	273,140	438,113	296,214	3,462	—
Russia	66,388	97,402	139,635	186,417	118,683	3,260	—
Sweden	42,586	24,959	22,967	21,170	14,429	11,441	1,465
Switzerland	50,629	43,667	47,353	55,793	20,022	27,568	29,922
New Zealand	—	—	—	—	37,220	11,233	—
				EXPORTATION			
Germany	399,144	360,909	499,406	713,878	307,106 six mths.	—	—
Austria	806	631	921	2,007	950	—	—
Belgium	426,669	416,318	550,841	685,907	335,017	—	—
France	—	—	—	—	237,492	4,367	4,046
England	—	222,324	198,987	167,749	134,392	119,230	39,248
Netherlands	88,704	57,775	128,693	197,854	139,764	368	—

the roots of plants only very slowly, and it is therefore advantageous to transform it into monocalcium phosphate, $CaH_4(PO_4)_2$ (superphosphate), which is soluble in water, and therefore easily dissolves in the soil and penetrates uniformly throughout all the strata of arable land. In contact with the lime in the soil it is transformed into dicalcium phosphate and also into tricalcium phosphate, insoluble in water, but it is then so uniformly distributed and so finely divided that it is carried to the root terminals and the juices of these attack and assimilate it rapidly. The solubility of superphosphate is, therefore, of advantage entirely and only because it temporarily facilitates this subdivision and penetration into the soil; when superphosphate and calcium cyanamide are mixed, the monocalcium is transformed into dicalcium phosphate.

Finely ground tricalcium phosphate or phosphorite may also be employed directly for peaty, marshy, and acid soils, or for other soils when an immediate effect is not required, but such effect is not comparable with that of superphosphate.

Superphosphates are the product resulting from the treatment of natural tricalcium phosphate with strong sulphuric acid in such a manner that the maximum amount of monocalcium phosphate soluble in water is obtained, together with a little dicalcium phosphate soluble in ammonium citrate, mixed with the crystalline gypsum which results from the reaction.

It was formerly thought that, to obtain a dry, pulverulent superphosphate, it was necessary that the calcium sulphate present should be in the form of gypsum ($+ 2H_2O$), and not of anhydrite ($CaSO_4$). Pratolongo (1916) showed, however, that most pulverulent superphosphates contain mainly anhydrite, whereas in bone superphosphates prepared with a limited proportion of sulphuric acid, gypsum often predominates. The monocalcium phosphate occurs almost always as hydrate, $CaH_4(PO_4)_2, H_2O$, but sometimes also as anhydrous salt.

It is known (J. Kolb, 1874) that the first phase of the reaction between sulphuric acid and tricalcium phosphate leads rapidly, at any rate as regards two-thirds of the phosphate, to free phosphoric acid: $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$, with generation of 64·4 cals. per 1000 grams of phosphate, and the mass is somewhat fluid (the phosphoric acid may, however, be derived from the monocalcium phosphate by hydrolysis). More heat is developed by the reaction between calcium carbonate and sulphuric acid: $CaCO_3 + H_2SO_4 = CO_2 + H_2O + CaSO_4$, 104 cals. being liberated per 1000 grams of the carbonate.[1] With a lower velocity, however, the phosphoric acid and calcium phosphate give monocalcium phosphate: $Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$. The resulting monocalcium phosphate contains, however, one molecule of water of crystallisation, and in a few days the whole mass becomes a spongy solid (owing to evolution of CO_2).

If an excess of sulphuric acid is employed, this remains free, and free phosphoric acid is also formed, whilst the resulting superphosphate is moist and forms pasty lumps.[2] If

---

[1] The African phosphorites (Gafsa and Kalaa Djerda) are richer in carbonates than the American and Oceanic, and although the carbonates (which give marked evolution of heat with sulphuric acid) accelerate the attack of the phosphorites, other factors also intervene to influence the velocity of the reaction (especially the thermal conditions of the process). Indeed this velocity is greater with phosphates relatively poor (*e. g.*, Land Pebbles) than with those rich in carbonates (*e. g.*, Gafsa), although phosphates such as apatite which do not contain sufficient calcium carbonate react with sulphuric acid with more difficulty because the mass does not become heated and a moister and less porous product results. In such cases it is necessary to work with hot acid or to admix phosphorite containing much limestone.

If the phosphorites contain fluorides (from 0·5 to 7 per cent.) or small quantities of chlorides, hydrofluoric or hydrochloric acid is formed by the action of the strong sulphuric acid, and since silicic acid is simultaneously liberated, gaseous silicon fluoride, SiF_4, finally results; this has an irritating smell and is obnoxious, and on discharge of the superphosphate from the chambers, it must be removed by fans or by absorption in water, as otherwise it would be harmful to the health of the workpeople and the vegetation of the vicinity.

[2] One of the most important practical requirements in a superphosphate is a high degree of fineness, on which depend the ease and uniformity with which it can be spread over the soil. According to Pratolongo (1916) the fineness is the greater, the lower the sum of the percentages of free phosphoric acid and free water (liquid phase of the superphosphate); if this sum exceeds 18 per cent., superphosphates begin to become only slightly powdery, while if it reaches 25 per cent. they are moist and readily become pasty when compressed. [The free phosphoric acid is taken as the acidity of the extract obtained with 95 per cent. alcohol (by vol.) in the cold, and the loss of weight of the superphosphate after extraction with alcohol gives the sum of the free phosphoric acid and free water.] According to Pratolongo the content in free phosphoric acid depends, besides on the proportion of sulphuric acid used, also on the temperature of reaction, best 80° to 100°. At higher temperatures, the final mass is less pulverulent as the quantity of

too small a quantity of phosphoric acid is used dicalcium phosphate is mainly formed which is insoluble in water, but soluble in ammonium citrate. Thus also, if unaltered tricalcium phosphate remains this forms dicalcium phosphate in contact with the monocalcium phosphate.[1] The iron in the phosphorite is partially obtained as primary phosphate, but in certain cases if the phosphates must be dried it reacts with the monocalcium phosphate forming insoluble ferric phosphate and thus diminishes the amount of soluble phosphate, that is to say, a *reversion* occurs which it is necessary to avoid by working with phosphorite containing little iron, and by regulating the temperature of drying of the superphosphate. This reversion also occurs in the soil, and in order to retard it, admixture of finely divided stable manure with the superphosphate has been proposed. With regard to yield, the superphosphate works calculate that about 2 tons of superphosphate are obtained from 1 ton of phosphorite.

The strength in phosphates is given in percentage of P_2O_5 soluble in water and in ammonium citrate, but 80 per cent. should be soluble in water. In the German and United States superphosphate trade the strength is given in phosphorus pentoxide soluble in water, and thus the same superphosphate will be indicated in Germany by a figure somewhat lower than that on which it would be sold in Italy and in England.[2]

---

free phosphoric acid increases and the water of crystallisation of the monocalcium phosphate is liberated and makes the mass moist.

According to Aita (1916), high pulverulent properties are more easily obtained by using sulphuric acid of 54° to 55° Bé. instead of 50° to 52°; he states that such properties are independent of the temperature of the reaction. He holds that the free phosphoric acid and water should not be determined by means of 95 per cent. alcohol, as this hydrolyses the monocalcium phosphate forming free phosphoric acid and insoluble dicalcium phosphate, the results being thus falsified. With anhydrous ether, however, more exact results are obtained (the free phosphoric acid found is about 50 per cent. less than with alcohol), and it is then found that all superphosphates are pulverulent which contain less than 2 per cent. of free phosphoric acid, whereas those with more than 4 per cent. readily become pasty. The moisture in a good superphosphate does not, in general, exceed 10 to 12 per cent.

[1] In superphosphate works the exact determination of the quantities of sulphuric acid which must be added to each type of phosphorite, including the amount consumed by the carbonates, fluorides, sesquioxides, etc., is of importance, and the water necessary to obtain a superphosphate containing 10 per cent. of moisture must also be determined.

The consumer pays only on the soluble phosphate, so that the amount of sulphuric acid to be used must be so chosen as to give the greatest proportions of phosphoric anhydride soluble in water (monocalcium phosphate), and in ammonium citrate (dicalcium phosphate). Well-prepared superphosphate contains less than 0·8 per cent. of insoluble P_2O_5.

In many works the quantity of sulphuric acid necessary for the decomposition of phosphorite is determined by Rümpler's method, by weighing out 20 grms. of powdered phosphorite, treating it with an exactly measured excess (for example, 20 c.c.) of sulphuric acid of 45° Bé., which has been accurately titrated, in a 1-litre measuring flask and digesting in a water-bath for two hours. After cooling, the whole is made up to 1 litre with water. It is then filtered and 50 c.c. of the filtrate are titrated with $\frac{N}{10}$ solution of sodium hydroxide until a turbidity commences to appear, showing that all the free sulphuric acid is saturated and that the reaction with monocalcium sulphate has started. By deducting the free sulphuric acid found from the quantity of acid employed, the quantity of acid necessary for treatment of the given phosphorite can be exactly calculated, although in the case of phosphorites rich in sesquioxides a little more than the calculated quantity is employed. Any tricalcium phosphate which may remain unaltered constitutes a loss to the manufacturer, because superphosphates are to-day sold according to the strength of P_2O_5 soluble in water and in ammonium citrate only.

To calculate rapidly and with fair approximation the quantity of sulphuric acid required to transform the phosphorite into superphosphate, use may be made of factors deduced from the chemical reactions, *e. g.*, $Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2$, and $CaCO_3 + H_2SO_4 = H_2O + CO_2 + CaSO_4$. Thus 1 kilo of tricalcium phosphate requires 0·632 of monohydrated sulphuric acid (equal to 0·947 kilo of acid at 53° Bé.), and 1 kilo of carbonate 0·980 kilo of the monohydrated acid (or 1·468 kilo of acid at 53° Bé.). In practice rather more than these quantities are taken, since the phosphorites contain also various substances which fix sulphuric acid (*e. g.*, fluorides, etc.), and for 1 kilo of the principal component Aita proposes the following practical factors: 1·14 kilo of sulphuric acid of 53° Bé. for tricalcium phosphate, 1·47 for the carbonate, and 3·34 for ferric oxide and alumina. Naturally, the physical characters of the phosphate are also of importance, so that a large-scale control experiment is made for each phosphorite, and the three factors corrected, if necessary, so as to give the maximum solubility. With sulphuric acid more concentrated than 55° Bé., the pasty mass sets too rapidly and is difficult to run out.

[2] *Preparation of the sample for analysis.* This is of great importance, and the sample should be removed from several sacks and at various depths from each sack by means of a sampling tube. These portions are then quickly mixed, giving about 1 kilo, which is divided and introduced

INDUSTRIAL PROCESSES. The natural phosphate in smaller or larger pieces, sometimes as gravel, is loaded loose into vessels and passes from these into trucks in which it is conveyed to the works. When it arrives in a very moist condition, which is rarely the case, it must first be dried in ovens. Ordinarily it contains from 1 to 3 per cent. of moisture, but not more than 5 per cent. can be tolerated because a larger quantity renders the subsequent grinding difficult.

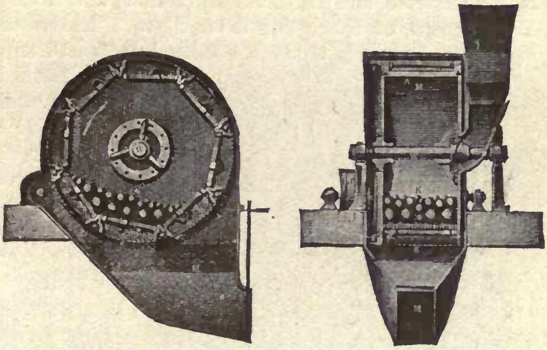


FIG. 251.

The lumps of phosphorite are first roughly crushed in a crusher (p. 292), which has an output of 3 or more tons per day. The material which has

into three dry glass bottles, preferably closed with glass stoppers or with a good cork stopper which should finally be paraffin-waxed. The stopper is tied down with a string, the ends of which are fastened and fixed to a label with a seal, and the stopper itself is also fixed with the seals of the buyer and the vendor.

On the label the statements referring to the contract and the quality and quantity of the product are given, and it is also inscribed with the testimony of the two parties who have assisted in removing the sample. The sample is sent to a laboratory selected by common accord for the execution of the analysis. The second sample may be eventually sent to another laboratory for control, and the third is reserved in case of disagreement between the results of the two first laboratories.

In the laboratory the chemist notes if all the seals are in order and enters the details on the label, and then if the superphosphate is dry it is passed through a sieve, any remaining lumps being broken up until the whole sample has passed through. If the sample is very moist, it is necessary to mix it by hand as well as possible.

Usually the determination of the phosphoric acid soluble in water and in ammonium citrate is of most importance, and sometimes also the total phosphate. The results are expressed as phosphorus pentoxide, P_2O_5, and the determination is made according to the official methods described in treatises on analytical chemistry.

In bone superphosphate the nitric, ammoniacal and organic nitrogen is determined.

The *Analysis of Basic Slag* is ordinarily confined to the determination of the degree of fineness and the percentage of total phosphoric acid, but it should be noted that in order to ascertain that the slag has not been adulterated with ordinary ground phosphorite, it is advisable always to determine the amount of phosphoric anhydride soluble in citric acid, which is always from 75 to 80 per cent. of the total anhydride in the pure slag, whilst in phosphorite it is only 10 to 12 per cent.

The fineness is determined by weighing the quantity of powder which remains on a Kahl No. 100 sieve (or French sieve) after sieving 50 grams of the slag for a quarter of an hour. This weight must be multiplied by 2 and subtracted from 100. A good slag has a degree of fineness of 80. These sieves do not, however, always yield concordant results.

We give here a Table of the French numbers for metallic gauze sieves. These may be transformed into English numbers by using the relationship between the French or Parisian inch (27·1 mm.) and the English inch (25·4 mm.); thus, No. 80 French sieve corresponds with No. 75 English.

No. of French sieve	No. of meshes per cm.	No. of meshes per sq. cm.	Thickness of wires in mm.	No. of French sieve	No. of meshes per cm.	No. of meshes per sq. cm.	Thickness of wires in mm.
4	1·4	2	—	60	22·2	493	0·167
6	2·2	5	—	65	24·0	576	0·155
8	2·9	8	—	70	25·9	671	0·143
10	3·7	14	—	75	27·8	773	0·134
15	5·6	31	—	80	29·6	876	0·125
20	7·4	53	—	90	33·3	1109	0·111
25	9·6	93	0·420	100	37·0	1369	0·100
30	11·1	123	0·333	110	40·7	1600	0·090
35	12·9	166	0·280	120	44·4	1970	—
40	14·8	219	0·250	130	48·1	2310	—
45	16·7	280	0·220	140	51·8	2685	—
50	18·5	342	0·200	240	88·6	7840	—
55	20·3	412	0·180				

thus been crushed must then be finely powdered and sieved. Among the many systems proposed for this purpose the best results are obtained with ball mills. In Figs. 251 and 252, transverse and longitudinal sections and a view of one of these mills are shown. They consist of a rotating drum 2½ to 3 metres wide and up to 2 metres in length, constructed of perforated steel or hardened cast-iron plates. They contain 2 to 3 tons of steel balls of varying sizes (from 5 to 12 cm. diameter). The drum is actuated by a 25 to 35 h.p. motor. The plates inside the drum are so arranged that they form steps at their junctions, and thus the balls which are carried round by the movement of the drum continually fall back on to one another below, hitting and pulverising the fragments of phosphorite until they acquire such a degree of fineness that they first pass through the holes in the plates and then partially through a fine sieve (No. 50) by which the plates are surrounded. The coarser portion, which does not pass through the sieve, is carried up by ledges to the top of the drum during its rotation and then falls back to the bottom through a slit which is suitably placed between one plate and another, so that it is again ground; 97 per cent. of a well-ground phosphorite passes through a sieve with 60 meshes to the inch. The fine powder which passes through the sieve gradually collects at a lower aperture closed by a flap. These mills have been greatly improved of recent years by various works (*see below*, Cement Industry). In many works Griffin mills are used with two or four pestles. Since 1905 the Kent mill has been widely used (Fig. 253); it consists of a large free grinding drum, *t*, which contains three revolving cylinders 1, 2, and 3; the upper cylinder, 1, rotates at a velocity of 180 revolutions per minute, and since it supports the grinding cylinder it causes this to revolve at 40 revolutions per minute, and the drum in turn causes the cylinders 2 and 3 to revolve by friction. All the cylinders are partially dependent on one another because they are connected with three steel springs, *m*, in such a manner that when one of them is displaced through the passage of an especially large or hard lump of phosphate the energy is recovered by pressure on the other cylinders and is thus not lost. The phosphate which has previously been coarsely ground is introduced into the mill at its two extremities by means of a hopper, *b*, and as it is pulverised it adheres to the internal surface of the grinding drum through centrifugal action, so that it is continuously carried round, and the continual grinding action of the particles on one another causes a very much finer grinding than is the case in ball mills. This machine also uses

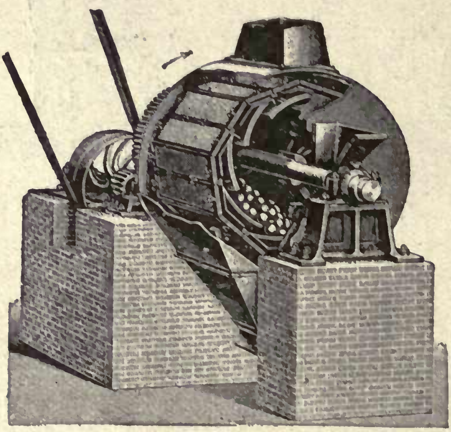


FIG. 252.

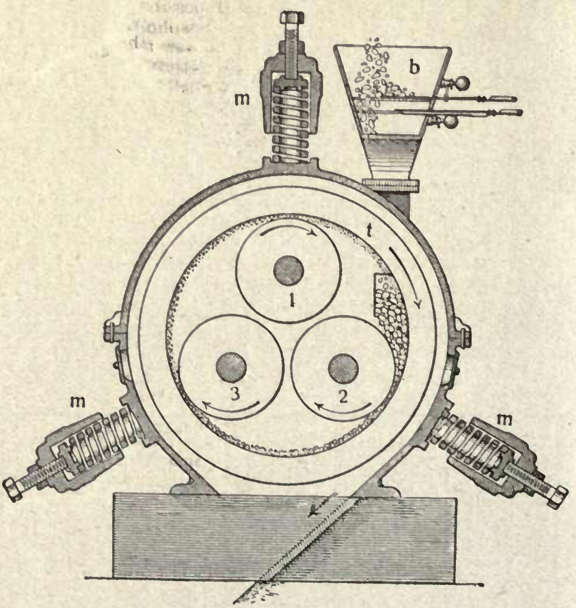


FIG. 253.

less power and is less rapidly worn. It has the additional advantage that the large amount of noise characteristic of ball mills is absent. The Kent mill is now also used in cement works. With phosphorites the sieves may be eliminated by using air separators, which separate the fine and coarse parts of the product just after grinding (*see* Cement).

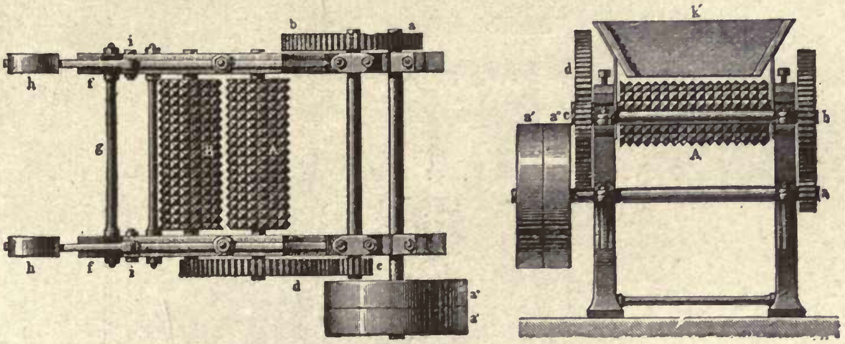


FIG. 254.

The treatment of bone is carried out with somewhat different machinery. The first crushing of the degreased bones is carried out between toothed cylinders such as are seen in plan and in elevation in Fig. 254. A further crushing is carried out in a stamp mill (Fig. 255) which breaks the bones upon a grating, allowing the smaller pieces to pass through. Below the grating there is a helical transmitter which carries the product to a grinding mill, which powders it, and after sieving it is treated in the same way as phosphorite.

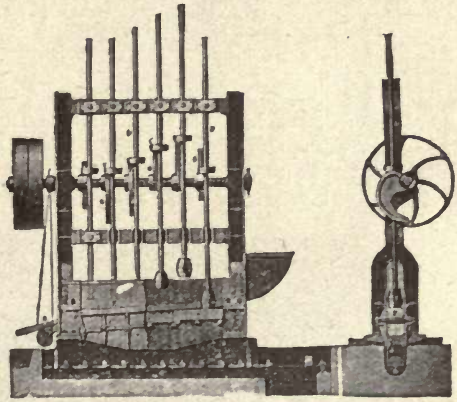


FIG. 255.

After the phosphate has been finely powdered it is treated with sulphuric acid in order to convert it into superphosphate. Superphosphate works ordinarily produce their own sulphuric acid, and employ one portion of it at 60° Bé. as obtained in the Glover tower and the rest at 52° Bé. as obtained directly in the lead chambers. It is always necessary to determine accurately the strength of the acid employed in order to be able to calculate the exact quantity required for a given weight of the previously analysed phosphorite.

The first reaction between the acid and the phosphate is carried out in a mixer.

The first types of mixing machine consisted of an inclined leaden cylinder (Fig. 256) containing a shaft provided with blades to mix the powder and the acid which were introduced into a hopper at the upper part and then discharged from the lower part into a chamber beneath ("pit" or "den"). To-day horizontal cast-iron mixers with blade stirrers are generally used.

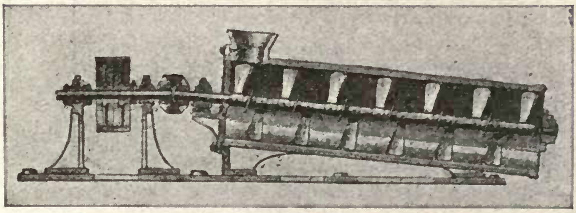


FIG. 256.

Lorenz employs a mixer with a special stirrer similar to the earth-board of a plough, which revolves rapidly so that complete mixing is attained in half a minute. The mixer, *a* (Fig. 257), is supported on a wall which separates the two pits which receive the superphosphate; it has two discharging openings, each communicating with one of these pits, *g*. Up to 8 tons of superphosphate can be produced per hour with a motive force of 2 h.p. Since the reaction occurs to a considerable extent in the mixer, in which the mass becomes hot and evaporates a little water, drier superphosphates are obtained by this method. The acid passes in directly from the lead chamber and the Glover tower and is brought to the required strength in the vat *k*. A smaller vat, *h*, measures off the necessary quantity of acid corresponding with the charge for each operation.

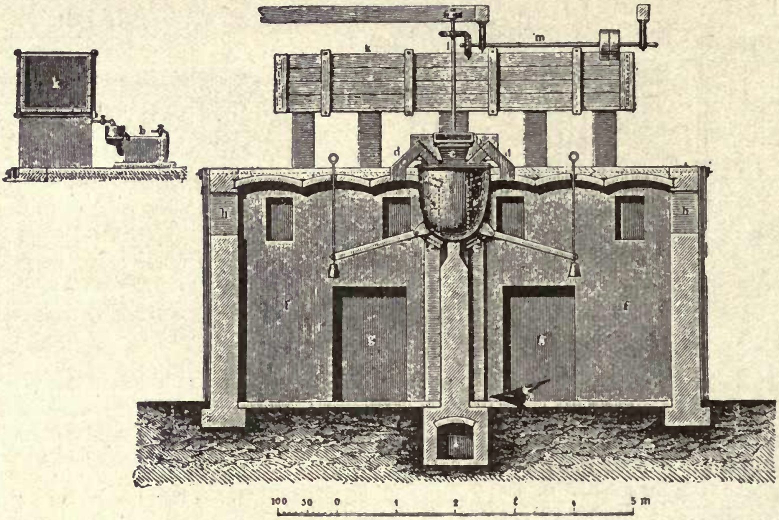


FIG. 257.

The superphosphate passes out of the mixer in an almost liquid condition and collects in horizontal layers in the pits until these are half filled, after which they are completely closed. In these pits the reaction between the sulphuric acid and the tricalcium phosphate is completed. The temperature rises considerably and much gas is evolved, consisting of carbon dioxide, silicon fluoride, hydrofluoric acid and hydrochloric acid. These gases escape through the outlet, *b*, and pass through it into the absorption tower. The loss in weight due to water vapour and to the various gases is 7 to 10 per cent.

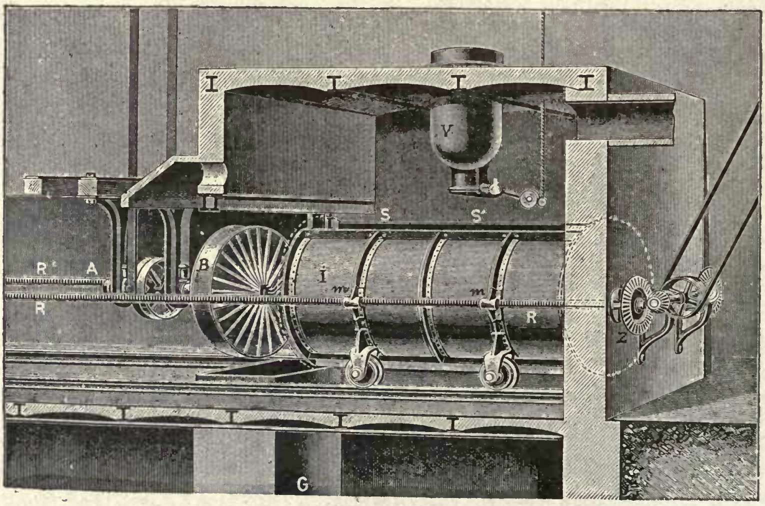


FIG. 258.

There are several adjoining pits divided by walls, and thus while one chamber is being filled the contents of a second are standing and a third is emptied, after which it is allowed to cool slightly. Each pit is capable of holding 50 to 100 tons of superphosphate. After 2 to 4 days the windows and discharging doors of the pits are opened. These apertures are closed before filling with bricks or with wooden boards which fit tightly and are plastered over with clay in order to prevent the gas from escaping. In some works the superphosphate is discharged after only twenty-four or thirty-six hours in order to powder and sieve it whilst still hot, and dry it by means of a current of air drawn over it with a fan in order to remove steam. The chambers are usually discharged by hand with pickaxes, and since the temperature of the mass is high and noxious gases are evolved a fan should be employed during discharging in order to draw the gases away into the flue leading to the absorption towers. The workmen wear clogs and are provided with masks containing a sponge moistened with dilute soda solution in order to preserve their lungs and eyes from the action of the poisonous gases. In better appointed works there are various mechanical appliances for the extraction of superphosphates from the chambers, thus avoiding any injury to the workmen and economising labour.

We illustrate Milch's apparatus, which is somewhat widely used in Europe, in Fig. 258. The maturing chamber, which collects the superphosphate paste, consists of a very large horizontal cast-iron cylinder, *i*, which may contain up to 30 tons of superphosphate and runs on wheels. The upper longitudinal portion of the cylinder, *S* and *S′*, and the diametrically opposite portion, consist of long slits which are closed by plates during filling; a single plate at the top is opened whilst the superphosphate paste is passed in from the mixer, *V*. When the whole mass contained in the cylinder has hardened (after three to four hours) it is removed from the inside of the chamber by causing two long horizontal screws, *R*, which carry sleeves, *m*, attached to the large cylinder, to revolve by means of the spur-wheel, *Z*. Then the plate which closes the mouth of the cylinder at the end, *i*, is opened and the surface of the hardened superphosphate is gradually pressed against the wheel, *B*, which carries metallic blades revolving rapidly over its surface; it is thus cut away and falls into a channel below, the plates which close the horizontal bottom of the cylinder being gradually removed. When the cylinder has been completely removed from the chamber and emptied in the manner described all the movements are arrested automatically.

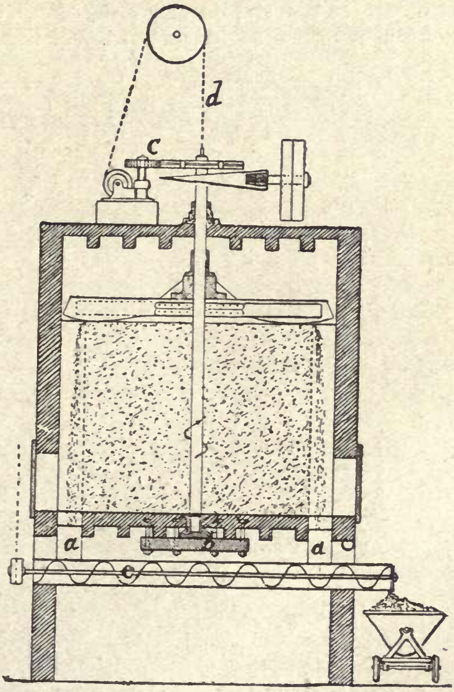


Fig. 259.

More economical, although less perfect in construction, are those of Alegri (Ital. Pat. 96,958) and of Pozzi di Vercelli, which are used in certain Italian works. During recent years increasing use has been made of the Poncioni system (little different from that of Hövermann, Ger. Pat. 196,938, Feb. 1907), which has the advantages of great simplicity and low cost, but the defect that the metallic mechanism is left continuously in contact with the fumes of the maturing pits. The Poncioni pit (Fig. 259) consists of a reinforced concrete cylindrical chamber, 3 to 4 metres in diameter. Before this chamber is charged with the superphosphate from the mixer, two wooden beams above the discharge orifices, *aa*, on the bottom are fixed at two opposite points on the periphery of the chamber. In the middle is fixed an axis which passes through the base and is carried below on a stout support, *b*, and is rotated by a toothed wheel, *c*, at the top; at the upper part of the axis inside the chamber are arms with horizontal or inclined blades. When the superphosphate has been charged into the chamber, and after due rest, the two wooden beams are withdrawn, two vertical channels ending below at the apertures, *a*, then remaining. When the axis is rotated, the blades scrape off the upper part of the block of superphosphate and force the abraded material to the periphery so that it falls into the vertical channels and thus into the horizontal screw, *e*, which carries it directly to the wagons taking it to the store. The motor, *c*, regulated by a cord, *d*, lowers the blades gradually as the surface of the block is scraped away.

A more perfect but more expensive mechanical extractor (£1400 to £1600, *i. e.*, about four times the price of the Poncini plant), which is largely used in all countries, is that of Keller (Ger. Pat. 189,245). On a long arm, *b* (Fig. 260), introduced into the top of the discharging chamber, runs an endless chain carrying alternate knives and scrapers (*a* and *c*), the abraded material being forced into the front part of the chamber, where it falls on to the trucks. The arm, *b*, is fixed to an iron framework, *f*, and a motor and suitable gearing allow of its horizontal and vertical displacement, so that the whole of the superphosphate may be scraped away. During the solidification of the superphosphate in the chamber, the arm and all the gearing remain outside. The iron framework is mounted on a truck, *v*, carried on wheels in front of the chamber.

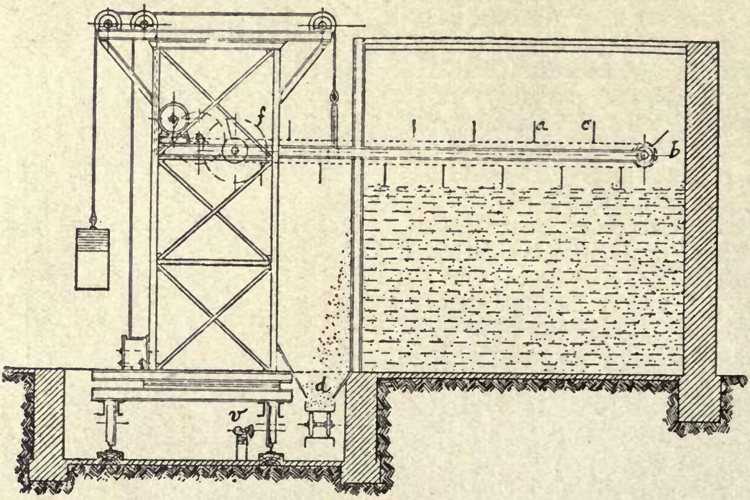


FIG. 260.

Another mechanical extractor in common use and costing about one-half as much as the Keller type is that of Wenk (Ger. Pat. 243,369), this resembling the Milch extractor (*see above*) in many points. Many other forms have been suggested, the principal being: J. Lorenz and J. Luetjens (Ger. Pat. 140,841), Svenska (Ger. Pat. 231,688), Binard (Ger. Pat. 257,191), Albert (Ger. Pat. 235,529), etc.

The gases from the maturing pits must be washed before they are allowed to escape into the atmosphere, as otherwise they would injure vegetation. For this purpose towers 8 to 10 metres high are used, down which a spray of water passes in a thin layer over cement plates and inclined planes arranged in such a manner that the gas pursues a zig-zag path in an opposite direction to the water. The gases may also be washed with an atomised water-spray obtained with a Körting apparatus in a series of special chambers which force the gases to pursue a lengthened path, and finally to escape free from harmful substances. All this plant, consisting of towers or chambers, is constructed in pitch pine, which is the most resistant wood, and the joints of the planks are made good with mastic, molten sulphur, pitch or bitumen, otherwise openings would easily form because fluosilicate solutions contract wood instead of causing it to swell.

The water in which the gas has been washed contains mainly hydrofluosilicic acid, H_2SiF_6 (up to 12° Bé.). It is either mixed with lime and discharged into watercourses, or mixed with a 10 per cent. solution of sodium chloride or bisulphate, and the sodium fluosilicate, Na_2SiF_6, allowed to deposit, separated in a filter-press and then dried, when it contains up to 98 per cent. of fluosilicate. This may be utilised in enamel factories, for the manufacture of opaque glass or of certain special tiles, and is sold at as much as £16 per ton. The superphosphate is hot when removed from the chamber and contains from 15 to 20 per cent. of moisture. It is in the form of lumps, and is powdered in a crusher formed of parallel vertical revolving discs carrying numerous pins arranged in concentric circles (Fig. 261, Th. Carr's disintegrator). These discs revolve in opposite directions.

Drying by heat, which is carried out in case the product is too damp through an error in manufacture, is a delicate operation, because when the hygroscopic water is evaporated the gypsum loses part of its water of crystallisation at 120° and may then cause reversion. The transformation of monocalcium phosphate into acid calcium pyrophosphate and then into calcium metaphosphate at 200° is most serious, without considering other causes of reversion: $4CaH_4(PO_4)_2 = 3CaH_2P_2O_7 + Ca(PO_3)_2 + 5H_2O$. Whilst superphosphates containing meta- and pyrophosphates show a smaller proportion of soluble phosphoric anhydride on analysis, these substances are slowly decomposed in the soil by the action of water and CO_2, and transformed into orthophosphates which are assimilable by the plants (Maercker).

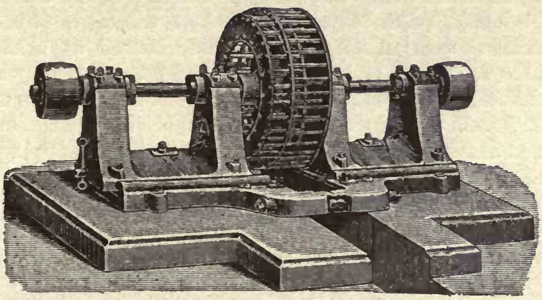


FIG. 261.

Of the various types of drying plants the best results are obtained with a long brickwork chamber (Fig. 262), in which Körting conveniently regulates the distribution of heat by flanged pipes. Small trucks which are introduced into the chamber are provided with finely perforated iron sheeting on which the superphosphate is distributed in thin layers. The trucks nearest to the source of heat are the first to dry, and whilst the trucks issue on one side with the dry product others with the moist product enter at the other, in such a manner that work is continuous and there is a rational utilisation of the heat. The gases which escape during drying should be led to the absorption towers.

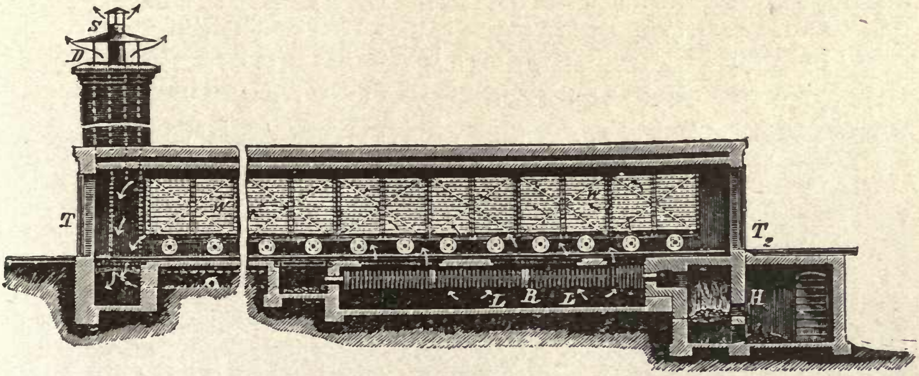


FIG. 262.

Superphosphate ready for sale is kept in storehouses protected from the rain, and is placed in sacks only at the moment of despatch, because these sacks are attacked in time by the acid in the superphosphate.

SUPERPHOSPHATES WITHOUT SULPHURIC ACID. Attempts have been made to manufacture superphosphate according to U.S. Pat. 978,193 (1910) by heating to redness in revolving furnaces phosphorite mixed with lime equal in amount to the total P_2O_5 present and with sodium and potassium carbonates corresponding with one-half the weight of the lime. In this way almost all the phosphoric anhydride in the state of phosphate should be rendered soluble in ammonium citrate. If it really gives superphosphate of high quality, such a method, which does not appear economical, might in some cases be suitable for treating low-grade phosphorites so as to obtain normal superphosphates.

Many years ago Wiborgh and Nilsson in Norway fused minerals poor in phosphate with soda so as to obtain rich superphosphates, but on an industrial scale the process was not economical, Norwegian and Swedish phosphates being too poor (*see also* U.S. Pat. 1,032,763 of 1912).

In 1910 a trial was made in Norway of the Palmer process for obtaining dicalcium phosphate (with 35 per cent. of P_2O_5 soluble in citrate) by treating the powdered poor mineral with chloric acid solution (formed by electrolysis of sodium chloride). The phosphate solution thus obtained was precipitated by addition of caustic soda, the sodium chlorate being thus regenerated. Such superphosphate is said to cost about £6 per ton. In normal times, however, rich phosphorites and sulphuric acid are obtained in abundance and at low prices, so that these processes can hardly be successful save in very exceptional cases.

Mention may be made of a new process proposed in Italy in 1914 for obtaining so-called tetraphosphate (?) simply by heating crude phosphorite in the hope that the phosphate would thus be rendered assimilable by plants and could thus replace superphosphates and basic slags. Chemical and crystallographic analyses by Menozzi in 1914–1916 showed, however, that the product differed from ground phosphorite only in dilution with sand. It contained about 19 per cent. of total P_2O_5, of which less than 1 per cent. was soluble in ammonium citrate; the calcium carbonate was almost entirely unchanged, so that the temperature attained was not very high.

This product was not very successful in Italy, in spite of recommendation by various more or less competent authorities. In 1917–1918 it appeared in France under the name *Italian Tetraphosphate* (!), but at the French Academy of Agriculture, Bruno and Cayeux expressed grave doubts as to its seriousness.

More promising is the attempt to prepare pyrophosphate by means of sulphur dioxide without making sulphuric acid.

The firm of Emilio Giana of Vercelli has manufactured calcium pyrophosphate on an industrial scale since 1908 by direct treatment of finely ground phosphorite at a high temperature (red heat) with sulphur dioxide in presence of air in furnaces similar to the Maletra furnace (p. 293) or in revolving drum furnaces like those used for cement (*q.v.*):

$$Ca_3(PO_4)_2 + SO_2 + O = CaSO_4 + Ca_2P_2O_7.$$

When ground this product forms a white powder of 96 per cent. fineness with Kahl's sieve; it has a natural reaction, does not corrode the sacks, and is very suitable for acid, humous, or siliceous soils. It contains 26·5 per cent. of total P_2O_5 and only 3 per cent. soluble in dilute citric acid, whilst 12 per cent. dissolves on prolonged contact with water and CO_2 (as in the soil). It becomes almost entirely soluble with one-third of its weight of sulphuric acid, which is the amount necessary to convert it into superphosphate. However, after a time the industrial preparation of this pyrophosphate was abandoned, in spite of the good results obtained in culture experiments and of the fact that the SO_2 used is only one-half of the amount necessary for the production of the corresponding quantity of superphosphate. A company which acquired the Giana patents did not begin to work on an industrial scale owing to insufficiency of capital, the patent rights in all countries being allowed to lapse. It is, indeed, difficult to compete with the superphosphate industry, for which there exist many plants technically simple and easy to work.

During the European War, to save sulphuric acid (especially in Germany) ammoniacal calcium superphosphate was prepared by saturating the superphosphate directly with the ammonia usually converted into agricultural ammonium sulphate. A sample had the percentage composition: total P_2O_5, 15·3; P_2O_5 soluble in ammonium citrate, 13·1; P_2O_5 soluble in water, 1·53; ammoniacal nitrogen, 6; the ammonia is fixed especially by the monocalcium phosphate and the phosphoric acid. Heating occurs during the reaction, this facilitating the drying of the product, which, however, shows a reversion of 50 per cent. in four months. Such a product could not, of course, be made in countries poor in ammonia.

Various mixtures of superphosphate with other fertilising salts are also prepared and also *double superphosphates* (of almost double the concentration of the ordinary product). These are obtained by treating tricalcium phosphate with phosphoric acid or a mixture of sulphuric and phosphoric acids, the last being obtained by washing with water freshly formed ordinary superphosphate, which is then rich in free phosphoric acid soluble in water (*Ducco*). Such double or triple superphosphates contain 25 to 45 per cent. of soluble P_2O_5, and before use are mixed with soil or inert matter.

STATISTICS AND PRICES. I. Production of *crude phosphate* (*phosphorite*). In 1910 the American product cost from 4*s.* 10*d.* to 7*s.* 2½*d.* per ton, according to strength, at Hamburg; the African product cost from 4*s.* 5*d.* to 5*s.* 7*d.* per ton.

Country	1898	1907	1909	1911	1913	1914	1915	1916
			PRODUCTION OF PHOSPHORITES (TONS)					
Belgium	200,000	181,230	205,260	196,780	219,420	14,000	—	—
Spain	—	3,078	1,387	3,520	3,548	8,312	9,080	14,111
France	350,000	375,000	397 908	312,204	335,000	130,000	—	25,000
Russia	—	16,774	21,522	25,737	25,000	15,000	—	—
United States	900,000	2,251,459	2,503,186	3,260,626	3,161,146	2,777,917	1,865,123	2,014,196
Japan	—	1,721	3,871	2,271	19,045	38,264	57,723	—
Christmas Island	—	110,000	197,982	250,000	152,405	95,284	24,119	—
Algeria	400,000	315,000	351,491	332,897	461,030	226,280	165,433	380,211
Egypt		—	1,000	6,425	104,450	71,945	82,998	125,008
Tunis		1,069,000	1,223,512	1,446,633	2,284,678	1,443,767	1,389,074	1,695,000
Pellew Islands	—	—	9,000	41,000	90,000	60,000 (half year)	30,000	—
Oceanic Islands and Nauro	—	190,000	197,922	250,000	—		—	—
			IMPORTATION OF PHOSPHORITES (TONS)					
Germany	—	579,505	663,400	833,260	928,798	420,165 (half year)	—	—
Austria-Hungary	—	123,497	172,934	172,538	203,028	128,180 (half year)	—	—
Belgium	--	—	—	195,214	244,767	113,668 (half year)	—	—
Denmark	—	—	35,651	20,082	55,876	49,301	—	—
Spain	—	78,710	82,697	163,651	254,463	202,051	212,085	288,328
France	—	636,549	645,177	740,357	940,791	661,429	325,762	285,906
Great Britain and Ireland	—	513,786	459,057	501,333	547,666	571,264	380,651	338,721
Netherlands	—	33,827	44,966	68,573	84,048	54,588	10,007	—
Russia	—	12,718	23,162	29,010	53,576	20,308	—	—
Sweden	—	92,577	75,095	91,425	123,250	90,864	39,105	82,820
Switzerland	—	16,516	22,580	19,247	18,885	17,964	10,939	7,457
Japan	—	128,280	71,065	230,273	331,288	285,097	135,767	99,702
Australia	—	39,099	51,108	87,437	162,599	89,397 (half year)	176,000	193,748

The *world's production of phosphorite* was 200,000 tons in 1886, 2,000,000 in 1898, 3,000,000 in 1904, 4,000,000 in 1906, 5,220,000 in 1908, 5,668,000 in 1911, and 6,500,000 in 1913.

Of the phosphorite imported into Italy, two-thirds originally came from Africa and one-third from America, but later three-fourths came from Africa (Gafsa, Kalae Djerda, and Constantine), containing 57 to 70 per cent. of tricalcium phosphate,[1] and one-fourth

[1] The Gafsa Company for the production of African phosphorite has a capital of £720,000, and is located at Tunis. It commenced by producing 65,000 tons in 1899; in 1901 it produced 178,000 tons, in 1905 524,000 tons, in 1907 746,000 tons, and in 1909 908,000 tons. Now that the railway which leads to the coast at Susa is finished, and the second pair of rails between Tunis and Kalae Djerda laid, this source of phosphates will acquire even greater importance. Tunis will be able to supply an abundance of phosphates for more than a century.

From Kalae Djerda 89,800 tons of phosphorite were exported in 1906 and about 192,000 tons in 1909, while the Société des phosphates tunisiens exported 236,000 tons in 1911. From Kalae Senam 98,000 tons were exported in 1906 and 334,000 tons in 1909. The Gafsa phosphorites are of two types, one containing 58 to 63 per cent. of tricalcium phosphate and the other 63 to 68 per cent., with a maximum of 14 per cent. of calcium and 2 per cent. of iron and alumina.

In the phosphorite industry various factors establish the commercial value and furnish the elements for rational working. The analytical statement must indicate the contents of tricalcium phosphate, iron and alumina (*ferral*), silicates, carbonates and moisture, as well as the price per 1000 kilos (African) or 1016 kilos (American), delivered c.i.f. Genoa. The seller always gives a discount of 2 per cent. (African) or 2½ per cent. (American).

Sampling: (1) Samples for analysis are usually taken on board during unloading in presence of buyer and seller. (2) The bag-samples are despatched to the analysts with certain precautions. (3) The samples are ground under definite conditions. (4) The first analyses, one by the buyer and one by the seller, are made in certain stated laboratories. (5) If the results of these two analyses differ, the deciding analysis is carried out in a stated laboratory. Every contract from America. Thus, in 1910, Italy imported 378,000 tons (407,000 in 1914), from Tunis, 19,000 tons (27,250 in 1914) from Algeria, and 24,000 (72,700 in 1914) from the United States. Whereas the total imports were 466,000 tons in 1912, 530,000 tons in 1913, and 514,000 in 1914, owing to transport difficulties they fell during the European War to 457,000 tons in 1915 and 431,500 in 1916, only 2300 tons coming from the United States. In 1917 a further diminution to 230,000 tons occurred owing to intensification of submarine warfare. The price of phosphorites was lowered by about 30 per cent. between 1907 and 1910, but it has gradually increased since 1911.

The African phosphorites are richer in calcium carbonate and poorer in fluorides than the American, which give superphosphates of higher grade.

In 1909 France produced 200,000 tons of Somme phosphates (which contain 70 to 75 per cent. of tricalcium phosphate, 3 per cent. of iron and alumina, and cost 7·6*d.* per unit of phosphate per ton in the ground condition, and loaded into trucks, early in 1910). American phosphate containing less than 5 per cent. of moisture costs £1 4*s.* to £1 8*s.* per ton of 70 to 80 per cent. strength f.o.b. at the port of departure. In France three-fourths of the production of superphosphate is provided by the numerous works of the "Société des produits chimiques de St. Gobain."

In Germany there are no phosphate deposits except a little apatite, now almost exhausted, in Saxony and Bavaria, and the phosphorites imported into Germany are supplied by the United States (60 per cent.), Algeria and Tunis (30 per cent.), and Belgium (about 10 per cent.); the imports amounted to 660,000 tons in 1909 and about 925,000 in 1913.

In 1908 England imported 530,177 tons of phosphorite, in 1909 451,800 and in 1910 455,500 tons. In 1908 Norway imported 976,000 tons.

In the United States of America in 1900 there were 422 chemical manure works with a capital of £12,000,000. In 1905 there were only 400 such works, but their total capital was £13,800,000, and they employed 14,200 workpeople and 1618 other employees. The production of phosphorite is very large, as much is exported.[1] In 1909 a Franco-American society in Tennessee commenced to exploit a deposit containing 25,000,000 tons. The phosphorite of Florida is always very rich in fluorides.

The amount of phosphorite utilisable in the future in the United States has been estimated as follows: 3,000,000 tons in South Carolina, 15,000,000 tons in Florida, 43,000,000 tons in Tennessee, and 100,000,000 tons in Idaho, Utah, and Wyoming.

In Mexico (Mazapil Valley) a deposit estimated at 20,000,000 tons of phosphorite with 52 to 66 per cent. of tricalcium phosphate was found in 1910.

The deposits in Tunis and Algeria are estimated at 12,000,000 tons.

The rapid development of the superphosphate industry is shown by the following table, giving the production in different countries in thousands of tons.

---

guarantees a certain minimum proportion of tricalcium phosphate. If this minimum is not reached, the buyer has the right to a bonus, varying in different contracts to an absolute minimum, below which the buyer has the right of refusing the material.

Iron and alumina (*ferral*): On account of the reversionary action of these elements in superphosphates, they are always allowed for in contracts. With American phosphorites a maximum of 2 per cent. of iron and alumina together is always guaranteed, whilst with African phosphates such maximum sometimes reaches 4 per cent. and is usually between 3 and 4 per cent. The rules as to sampling are the same as those for the phosphate determination. Here, too, if the maximum is exceeded the buyer is allowed two units of phosphate per one unit of ferral, there being also an absolute maximum beyond which the material may be refused.

Silicates: Whereas formerly this element was neglected, recent investigations have shown that its influence on reversion is greater than that of alumina and iron.

Moisture, etc.: A bonus is allowed when a certain percentage (usually five) of moisture is exceeded. The necessary samples are taken on board during unloading in presence of buyer and seller or their agents.

[1] The production of phosphorites in the United States is distributed as follows (tons):

		1909	Price per ton	1910	Price per ton
Florida	Hard Rock .	513,585	31·36*s.*	438,347	27·84*s.*
	Land Pebble .	1,266,117	14·24*s.*	1,629,160	13·72*s.*
S. Carolina	Land Rock .	201,254	17·64*s.*	179,659	16·32*s.*
	River Rock .	6,700	13·12*s.*	—	—
Tennessee	Brown Rock .	266,298	14·36*s.*	329,382	15·32*s.*
	Blue Rock .	66,705	16·48*s.*	68,806	14·00*s.*

Hard Rock contains 76 to 80 per cent. of tricalcium phosphate, Land Pebble 68 to 73 per cent., and Brown Rock 78 to 80 per cent.

Country	1900	1904	1908	1910	1912	1913	1914	1915	1916
United States .	1600	1900	—	2349	—	3248	3785	2533	—
France . . .	1150	1250	1850	1634	1950	1900	1600	600	350
Denmark . .	—	—	59	50	—	90	80	—	—
England . .	750	800	937	956	840	820	—	685	—
Germany . .	650	1000	1191	1387	1718	1819	—	—	—
Sweden . . .	—	—	150	167	168	184	188	155	—
Holland . .	—	—	—	306	—	—	350	100	40
Belgium . .	200	—	335	395	450	450	—	—	—
Austria-Hungary .	200	—	264	350	397	400	—	—	—
Russia . . .	—	—	80	88	205	—	—	—	—
Japan . . .	120	—	—	—	—	—	—	—	—
Spain . . .	—	—	180	208	210	225	220	194	315

The world's production of superphosphate in 1904 exceeded 6,000,000 tons, and was 7,500,000 tons in 1906, about 9,000,000 tons in 1910, and about 10,000,000 tons in 1913.

Italy produced only 72,000 tons of superphosphates in 1893, more than 150,000 tons in 1895, and 350,000 tons in 1900. Further, in 1907 50,000 tons of bone superphosphate were produced, in 1910 31,536 tons, and in 1915 31,455 tons.

Germany produced 1000 tons of superphosphates in 1867, only 7600 tons in 1872, and about 400,000 tons in 1883 (*see above*). There were about 140 superphosphate factories in Germany in 1912.

Spain has important superphosphate works in the provinces of Malaga and Seville and in the neighbourhood of Barcelona. Before the European War large amounts of superphosphate were imported (*see* Table, *later*), but the importation then rapidly diminished.

The Argentine possesses only two small superphosphate works and imports very little (567 tons in 1910).

Before the European War there were thirty-three superphosphate factories in Belgium.

In 1911 Russia imported 160,000 tons of superphosphate, 93,000 tons from Germany.

France exported 228,000 tons of superphosphate in 1909, 145,226 in 1913, 117,231 in 1914, and 59,818 in 1915.

The price of mineral superphosphate in Italy varies irregularly from 2·9*d.* to 4·8*d.* per kilo of P_2O_5 soluble in water and in ammonium citrate contained in 100 kilos of the superphosphate.

Importation and exportation of superphosphates are limited, as it is a product of little value compared with the weight, and thus cannot carry heavy transport charges.[1]

[1] Movement of Superphosphates (Tons)

Exporting Country	1907	1909	1911	1913	1914	1915	1916
			Exportation				
Germany . .	115,046	168,746	221,766	282,653	192,145 (½ year)	—	—
Austria-Hungary	246	929	3,907	3,748	1,971 ,,	—	—
Belgium . .	213,741	348,311	329,816	318,922	171,390 ,,	—	—
France . .	198,162	227,839	250,046	145,228	117,231	59,823	12,363
England . .	—	143,691	162,022	64,499	67,111	69,781	14,760
Netherlands .	132,735	232,300	280,286	352,849	269,386	4,626	—
Sweden . .	21,606	17,245	61,187	36,037	41,842	17,815	191
Japan . .	8,823	6,348	15,649	18,736	19,411	37,561	71,509
Australia . .	9,903	11,986	10,207	13,088	1,849 (½ year)	15,803	41,828
			Importation				
Germany . .	62,877	80,212	71,119	53,193	29,225 (½ year)	—	—
Austria-Hungary	48,757	67,389	62,216	75,224	43,993 ,,	—	—
Belgium . .	29,117	63,576	69,593	28,012	31,435 ,,	—	—
Denmark . .	—	—	87,291	110,151	142,883 ,,	—	—
Spain . .	143,434	177,431	258,562	150,235	116,897 ,,	64,245	23,115
France . .	66,288	123,448	79,384	100,822	58,155 ,,	14,038	4,122
Netherlands .	154,892	214,369	273,372	270,378	206,708 ,,	50,551	—
Russia . .	39,961	75,323	154,725	196,859	122,442 ,,	52	21
Australia . .	39,649	38,483	63,751	27,138	41,448 (½ year)	25,522	2,936
New Zealand .	—	—	—	—	57,042 ,,	55,121	—

The consumption of Basic Slag in Europe was in 1885 5000 tons, almost entirely in Germany, of the value of £1600; in 1891 400,000 tons; in 1899 1,655,000 tons (895,000 in Germany), of the value of £2,120,000; in 1907, 2,600,000 tons (1,500,000 in Germany), and in 1911, 3,263,000 tons (2,160,000 in Germany).

Italy imported 70,000 tons in 1902, 67,460 tons in 1905, 81,840 tons in 1906, more than 129,000 tons in 1907, and about 93,000 tons in 1909, of which two-fifths came from Belgium, one-tenth from Germany, and one-fifth from England.

The statistics of production, importation, and exportation of basic slag are given on p. 618.

STRONTIUM: Sr, 87.6

This element is not very abundant in nature and is found in combination as carbonate in *strontianite*, $SrCO_3$, and as sulphate in *celestine*, $SrSO_4$. It was studied as an element as early as 1792 by Hope, who obtained it free by electrolysing molten strontium chloride in presence of ammonium chloride. It is obtained also by heating a saturated solution of $SrCl_2$ with sodium amalgam and then distilling the mercury from the strontium amalgam so formed.

It is a shining yellowish metal of sp. gr. 2·5. It decomposes water at the ordinary temperature; it oxidises in the air and burns with a reddish flame. The heat of formation of the divalent $Sr^{\cdot\cdot}$ ion is 501 Kj.

STRONTIUM OXIDE : SrO. This compound is formed by heating the nitrate to redness or the carbonate to a white heat, or perhaps preferably, by heating a mixture of strontium carbonate and carbide: $3SrCO_3 + SrC_2 = 4SrO + 5CO$.

Strontium oxide dissolves in water with evolution of heat and formation of the hydroxide.

STRONTIUM HYDROXIDE : $Sr(OH)_2$. This is obtained directly by heating the carbonate with carbon in presence of steam, which diminishes the partial pressure due to the CO_2 by carrying it away, and thus causes the carbonate to dissociate more easily: $SrCO_3 + C + H_2O = 2CO + Sr(OH)_2$. Industrially almost all strontium compounds are prepared by reducing strontium sulphate to the sulphide by heating with carbon and then transforming this sulphide into other compounds by suitable reagents. The oxide, for example, is obtained by heating the sulphide in steam, or preferably by heating the sulphide solution with copper oxide: $SrS + CuO = SrO + CuS$. The hydroxide is strongly basic in aqueous solution and it crystallises with $8H_2O$ from the saturated solution. It has an important application in the extraction of the sugar of beetroot molasses, which contain 45 to 50 per cent. of sugar. This sugar cannot be recovered by crystallisation on account of the numerous impurities in the molasses. Strontium salts, however, form insoluble saccharates which separate and are then decomposed by carbon dioxide with formation of sugar and strontium carbonate, which latter can be used for the production of fresh hydroxide. This process is used in Germany, whilst the Italian sugar-works used baryta before the fiscal legislation of 1903 (*see* Sugar, Vol. II., "Organic Chemistry").

Strontium hydroxide for industrial use costs £14 per ton; when free from iron £18 per ton, and chemically pure for the laboratory 2*s.* 5*d.* per kilo.

STRONTIUM PEROXIDE : SrO_2. The corresponding hydrate is first prepared by the action of hydrogen peroxide on a solution of $Sr(OH)_2$; at 100° this hydrate forms H_2O and SrO_2, which separates as a white powder.

STRONTIUM CHLORIDE : $SrCl_2$. This is obtained by treating the carbonate or sulphide with HCl; it crystallises with $6H_2O$, and the white crystals are hygroscopic, readily soluble in water and also in alcohol, by which means it can be separated when present together with barium chloride. It is used for fireworks, and costs £30 per ton.

STRONTIUM NITRATE : $Sr(NO_3)_2$. This compound is obtained by treating the carbonate or sulphide with nitric acid. It forms colourless crystals, soluble in water and almost insoluble in alcohol, by which means it can be separated from calcium nitrate, which is soluble. It may also crystallise with $4H_2O$. It is used for fireworks for obtaining a red light, and costs £26 per ton.

STRONTIUM SULPHATE : $SrSO_4$, is found naturally as *celestine* in rhombic crystals isomorphous with anhydrite, $CaSO_4$. It is only slightly soluble in water (1 : 7000), and the solubility is diminished by the addition of alcohol. Celestine containing 95 per cent. of sulphate costs about £3 per ton, whilst pure strontium sulphate obtained by precipitation costs ten times as much. England produced 14,042 tons of the sulphate in 1909 and 4761 tons (£3600) in 1910.

STRONTIUM CARBONATE : $SrCO_3$. As the mineral *strontianite* this is found crystallised in the regular system, and is isomorphous with *aragonite*, $CaCO_3$. It may be prepared from the sulphide with CO_2, or by precipitating soluble strontium salts with sodium carbonate, also by melting strontium sulphate with Na_2CO_3. At 1100° the carbonate dissociates into $SrO + CO_2$; it is almost insoluble in water.

BARIUM: Ba, 137·37

This element is fairly abundant in nature in the form of *Heavy Spar*, $BaSO_4$, and as *Witherite*, $BaCO_3$, which yields the various salts of barium with the corresponding acids, whilst heavy spar must be reduced to the sulphide by heating it with carbon before other barium salts can be obtained from it. All barium salts soluble in water are poisonous. Barium is obtained in the metallic state by the electrolysis of molten $BaCl_2$ in presence of NH_4Cl, or, in the same manner as strontium, from barium amalgam, but the new electrolytic process of preparation from $BaCl_2$ solution, in which mercury is used as a cathode and forms an amalgam, appears to be better. The amalgam is then distilled in a current of hydrogen, the barium hydride thus formed losing H when heated *in vacuo*, so that pure barium remains (Güntz, 1907). It is also obtained by heating barium oxide with magnesium:

$$BaO + Mg = MgO + Ba;$$

better, according to Güntz (1906) thus: $3BaO + 2Al = Al_2O_3 + 3Ba$, or more economically (C. Matignon, 1913) by placing compressed pastilles of a mixture of barium oxide and powdered silicon (or ferrosilicon) in a steel tube, evacuating the latter and heating it, inside a porcelain tube, in an electric furnace at 1200°: $3BaO + Si = BaSiO_3 + 2Ba - 18,500$ cals.; the barium vapour condenses in the cold part of the steel tube outside of the furnace. The product thus obtained is 98·5 per cent. pure.

Pure barium has a metallic appearance with a yellowish reflex and a specific gravity of 3·75, melts at 1150°, and decomposes water more energetically than calcium and strontium.

Metallic barium has no practical application. If it could be obtained at a lower price it might be used as a dehydrating agent, as it decomposes water with great ease, and it might also be used in fireworks. The impure product obtained from sodium amalgam formerly cost 6*s.* per gram, whilst the pure, electrolytic product cost 28*s.*; now, however, it is much cheaper.

BARIUM OXIDE : BaO. This was once obtained by heating barium nitrate or hydroxide to redness. Frank (Ger. Pat. 135,330) prepared it by mixing a barium salt, $BaCO_3$, with barium carbide and heating the mixture out of contact with the air: $3BaCO_3 + BaC_2 = 4BaO + CO_2$. For the preparation of the peroxide it is indispensable, but not easy, to obtain highly porous oxide. The decomposition of the carbonate by heat, $BaCO_3 = BaO + CO_2$, is reversible and gives a non-porous product; the reverse reaction may be prevented by addition of carbon, which reduces the CO_2 to CO, but the presence in the carbon of hydrogen or moisture must be avoided so that $Ba(OH)_2$ may not be formed (W. Feld).

Egly (1905) obtains the porous oxide by heating to redness a mixture of barium carbonate and nitrate containing a little hydrocarbon. At Niagara Falls the oxide is industrially obtained in the electric furnace from a mixture of 4 molecules of $BaSO_4$ with 5 atoms of carbon in the form of coke (Brandley and Jacobs, Ger. Pat. 111,667); the product of the reaction contains 60 per cent. BaO and 40 per cent. BaS, while SO_2 is evolved, The oxide and sulphide are then transformed into barium hydroxide, which is largely used (*see below*).

Commercial barium oxide forms a greyish-white mass, sometimes in translucent cubes; its density is 5·7. Its heat of formation from the elements is 124,240 cals. At 2000° it is completely fused. It does not conduct electricity, and absorbs moisture eagerly with strong heating.

The crude 98 per cent. product costs £48 per ton and when purified £96, while the chemically pure oxide costs 5*s.* 6*d.* per kilo.

BARIUM HYDROXIDE : $Ba(OH)_2$. This compound is formed with evolution of heat on dissolving the oxide in water. It is also obtained from the carbonate and from the sulphide in the same manner as has been described for strontium hydroxide, or by reducing the sulphate with carbon and treating the barium sulphide so formed with CuO : copper sulphide and barium oxide are thus produced. On lixiviating, the oxide dissolves to form barium hydroxide, and the copper sulphide is then reconverted into copper oxide. It has been observed that the copper sulphide easily retains much barium hydroxide, which is then transformed into carbonate or sulphate and renders the regeneration of the copper oxide difficult, so that it becomes necessary to decompose the copper sulphide by wet methods. The copper oxide may also be replaced by zinc oxide.

In America it is obtained from barium sulphate by the Brandley and Jacobs process (*see above*), by lixiviation with water of the product from the electric furnaces containing 60 per cent. BaO and 40 per cent. BaS. All the oxide and one-half of the sulphide are converted into the hydroxide: $2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2$. From the hot solution the almost pure hydroxide (less than 1 per cent. of impurity) crystallises on cooling, while the mother-liquor contains the barium hydrosulphide.

Barium hydroxide is also prepared by transforming the sulphide into carbonate by means of CO_2 and H_2O and then preparing the carbide from it by heating with carbon in the electric furnace. With water the carbide forms barium hydroxide and acetylene, which may also be utilised:

$$BaC_2 + 2H_2O = Ba(OH)_2 + C_2H_2.$$

Attempts have also been made to electrolyse a solution of barium sulphide directly.

The hydroxide is soluble in water, forming a strongly alkaline liquid, and crystallises with $8H_2O$, but loses $7H_2O$ in the air, whereas the last molecule of water is expelled only at a dull red heat; at a white heat BaO is formed. It melts at 78° and fixes CO_2 easily from the air. 100 parts of water dissolve 1·5 part of the hydroxide at 0°, 2·9 at 15°, 11·75 at 50°, or 90·8 at 80°. Barium hydroxide is used in large quantity for the extraction of sugar from molasses, as has been explained in the case of strontium hydroxide. The crude commercial crystalline product costs £15 4*s.* per ton, the anhydrous product £46 8*s.*, and the chemically pure anhydrous product costs 2*s.* 5*d.* per kilo.

Since 1903 barium hydroxide has not been used in Italy for the extraction of sugar from molasses because this sugar extracted from molasses is no longer exempt from taxation, as was formerly the case (*see* Vol. II., "Organic Chemistry," Sugar). In 1902 Italy produced about 3615 tons, in 1903 only 412 tons, of the value of £3920, in 1904 about 70 tons, of the value of £504, in 1907 about 613 tons, in 1908 about 450 tons, of the value of £4000, in 1913 50 tons, in 1914 136 tons, and in 1915 227 tons. The imports were 564 tons in 1908, 1889 in 1910, 118 in 1912, 136 in 1913, and 222 in 1914, but in 1915, 1916, and 1917, 62, 31, and 19 tons respectively were exported.

In the United States 50,500 tons of barium hydroxide were produced in 1903, and only 22,500 tons, of the value of £15,000 in 1904.

BARIUM PEROXIDE : BaO_2. This is obtained from the oxide by heating to about 500° in presence of air. At higher temperatures the peroxide loses oxygen (*see* p. 196). The crude product forms a greenish mass, but when pure it is a colourless powder insoluble in water and forms hydrogen peroxide with dilute acids. On heating, it evolves oxygen, and is also used as a bleaching agent.

Barium peroxide, like other peroxides, such as hydrogen peroxide, Na_2O_2, etc., contains the group —O—O—, which is relatively unstable, and this explains the oxidising and reducing power of peroxides in general.

The anhydrous commercial peroxide of 85 to 89 per cent. costs £40 per ton, and the pure product £72. In 1905 Italy produced 60 tons, which enjoyed a protective tariff of £4 per ton, equal to that on the oxide; in 1910 the output was 25 tons and in 1911 25 tons. The United States imported barium peroxide to the value of £50,480 in 1912. France exported 659 tons in 1913, 543 in 1914, and 223 in 1915.

Germany exported 567 tons in 1908 and about 780 tons in 1909, and imported 170 tons; in 1911 the exports were 1456 and the imports 89 tons.

The world's production of barium peroxide in 1913 was estimated at 10,000 tons.

BARIUM CHLORIDE : $BaCl_2$. This compound crystallises in square plates of the rhombic system with $2H_2O$, and is not hygroscopic, as are $CaCl_2$ and $SrCl_2$. It loses water at 60°, and then melts at about 800°; at the melting-point in presence of steam it gives HCl. It is prepared from the carbonate with HCl, or preferably from the sulphide, BaS, by heating it with a metallic chloride, such as $CaCl_2$ or $FeCl_3$; thus by Kolb's method a mixture of 100 parts of barium sulphate, 36 parts of lean coal, and 68 parts of calcium chloride in very concentrated solution is heated in a furnace to 900°; the chloride is then dissolved with hot water.

A good mass fused in four hours contains 50 to 56 per cent. of $BaCl_2$ and less than 1 per cent. of sulphur (more indicates that too much coal has been used). The lumpy mass is lixiviated with hot water and CO_2 is passed through the solution at 24° Bé. until it ceases to give the reaction for sulphides (with lead acetate); the liquid is allowed to stand to clarify, and is then neutralised with hydrochloric acid and concentrated to 30° Bé. in enamelled iron vessels. When the solution cools, crystals of $BaCl_2 + 2H_2O$ separate. The reaction may be represented thus: $BaSO_4 + 4C = 4CO + BaS$; $BaS + CaCl_2 = CaS + BaCl_2$. The mother-liquor containing $CaCl_2$ serves for fresh fusions.

When calcium chloride is not available, barium chloride is prepared by treating barium sulphide (from the sulphate and carbon) with the calculated quantity of hot dilute hydrochloric acid.

Pure barium chloride free from iron and copper is not coloured by ferrocyanide or ammonium sulphide. To rid it from $CaCl_2$ it is re-crystallised from water and a little HCl (which diminishes the solubility) and the iron may be eliminated by adding to the solution a little barium carbonate or sulphide.

According to Ger. Pat. 257,277 (1911), if powdered barium carbonate is boiled and shaken for some hours with excess of calcium or magnesium chloride in concentrated solution, 95 per cent. of the carbonate may be transformed into barium chloride which may be extracted from the mass by means of water: $BaCO_3 + CaCl_2 = CaCO_3 + BaCl_2$.

H. Kühne (Ger. Pat. 243,074, 1911) proposed to manufacture $BaCl_2$ by fusing barium sulphate directly with magnesium chloride: $BaSO_4 + MgCl_2 = MgSO_4 + BaCl_2$. The reaction is, however, reversible, so that the mass must be cooled rapidly, magnesium sulphate then separating out, as it is less soluble than $BaCl_2$. The equilibrium of the system, $2NaCl + Ba(NO_3)_2 \rightleftarrows 2NaNO_3 + BaCl_2$, in aqueous solution has also been studied, but it does not seem to be of practical importance.

It is used for the prevention of boiler scale, for the preparation of precipitated barium sulphate, and as an addition to ceramic materials (bricks, etc.) in order to prevent the efflorescence of soluble sulphates contained in the prime materials. The commercial crystallised chloride costs £6 to £7 4*s.* per ton, and when purified £12 16*s.* Italy produced 490 tons in 1905, 600 tons in 1906, 800 tons in 1907, 950 tons (of the value of £7600) in 1908, 772 tons in 1910, 904 tons in 1911, 679 tons in 1912, 690 tons in 1913, 876 tons in 1914, and 1034 tons in 1915.

Germany exported 5340 tons and imported 1910 tons in 1909; in 1911 the exports and imports were 6179 and 2000 tons respectively, and in 1912 7297 and 3674 tons.

The United States imports in 1912 were valued at £5531.

BARIUM NITRATE : $Ba(NO_3)_2$. This is obtained by dissolving witherite in nitric acid or by treating a solution of $BaCl_2$ in the hot with sodium nitrate, as the barium nitrate, which is comparatively insoluble, then separates on cooling. According to Puls and Krug (Ger. Pat. 198,861, 1907), the pure nitrate is obtained in solution by heating a mixture of finely powdered barium carbonate with a solution of calcium nitrate in an autoclave at 4 atmos.; undissolved $CaCO_3$ finally remains. H. Kühne (Ger. Pat. 248,524, 1911) suggests fusing barium sulphate with twice the theoretical quantity of calcium nitrate: $BaSO_4 + Ca(NO_3)_2 = CaSO_4 + Ba(NO_3)_2$; when the mass is cooled and extracted with water, 75 per cent. of the theoretical yield of barium nitrate is obtained. Barium nitrate forms shining octahedral crystals which are only slightly soluble in water (7 parts in 100). At a red heat it decomposes, forming BaO.

It is still much used for the manufacture of the peroxide and as a component of certain sporting powders, and is also used for fireworks in order to obtain a green flame. It costs about £20 per ton. Italy produced 90 tons in 1907, of the value of £2160, 80 tons in 1914, and 31 tons (£1028) in 1915, and Germany exported 613 tons in 1909, 928 in 1911, and 798 in 1912.

BARIUM SULPHATE : $BaSO_4$. This compound is found in nature as *barytes* or *heavy spar* in rhombic prisms, isomorphous with celestine and of sp. gr. 4·6. It abounds in England, Germany, Hungary, Bohemia, Belgium, France, the United States, Canada, and in parts of Italy. When produced artificially it is employed as a pigment under the name of *permanent white*, and has to some extent replaced white lead (lead carbonate) because it is not poisonous and does not blacken with hydrogen sulphide or metallic sulphides, although its covering power is less. Natural barium sulphate is also used as a pigment after grinding it very finely, but it is not so valuable as that obtained by precipitation. The well-powdered natural sulphate is mixed with charcoal and heated to bright redness. The mixture of barium sulphide and oxide thus formed is dissolved in water, filtered and treated with sodium sulphate. Barium sulphate is precipitated and sodium hydroxide remains in solution. The sulphur dioxide formed in the furnace in which the sulphate is heated with charcoal is utilised for the preparation of Na_2SO_4 by Hargreaves' process.

If barium carbonate (witherite) is used as a raw material, it suffices to dissolve it in hydrochloric acid and precipitate with sodium sulphate or dilute sulphuric acid in the cold. When mixed with zinc sulphide it forms lithopone (*see* Zinc Sulphide).

It is insoluble in water (1 part to 430,000), and also in acids, and for this reason it is used in analytical chemistry for the separation of barium from soluble salts by precipitating it in the form of sulphate. It melts at 1580°.

Ground barium sulphate is also used to give consistency and weight to paper and cardboard, to adulterate mineral pigments and flour, and to form the rind of certain cheeses such as Gorgonzola (this use is now prohibited in France); further, it is employed in preparing articles of white rubber, artificial ivory, and asbestos cement.

The dry, commercial, precipitated sulphate (fixed white) costs £9 12*s.* per ton and in paste form of first quality £12. The second quality costs £6 and finely powdered natural barytes £4.

The production, importation, and exportation of precipitated barium sulphate in Italy is as follows (tons):

	1902	1904	1906	1908	1910	1912	1913	1914	1915	1916	1917
Production	220	—	—	56	563	422	49	100	90	—	—
Imports	1170	1875	1400	1523	1776	1986	1760	1408	1319	1398	1121
Exports	—	—	147	724	150	381	234	210	3288	2755	1112

The production of heavy spar was 14,420 tons in 1910, 13,620 in 1911, 13,420 in 1912, 12,970 in 1913, 12,970 in 1914, 17,850 (£15,600) in 1915, and 16,903 in 1916.

The barium sulphate produced in the United States amounted to 80,000 tons in 1906, 150,000 in 1907, 54,000 (£40,000) in 1908, 39,000 in 1910, 35,000 in 1911, and 34,000 (£30,680) in 1912, the bulk being supplied by Missouri, and containing 95 to 98 per cent. $BaSO_4$ and 1 to 3 per cent. SiO_2. The United States imported in 1911 18,200 tons, and in 1912 23,600 tons (£10,520) of crude heavy spar, besides 3300 tons (£5000) of ground heavy spar, and permanent white to the value of £14,000.

Germany exported 8455 tons of permanent white in 1907, 4888 in 1909, 6834 in 1911, and 8242 (£48,000) in 1912.

England imported 45,000 tons of heavy spar in 1910 and 48,300 (£134,520) in 1911, when 8400 tons were exported.

France imported 15,884 tons of barium sulphate in 1913, 10,163 in 1914, and 633 in 1915.

Barium Persulphate : $BaS_2O_8 + 4H_2O$, is obtained by electrolysing barium sulphate mixed with sulphuric acid.

BARIUM SULPHIDE : BaS, is obtained by heating barium sulphate mixed with coal, tar, or oil in a furnace at 600° to 800° : $BaSO_4 + 2C = BaS + 2CO_2$; at a higher temperature 4C reacts and CO is formed instead of CO_2. The mixture of sulphate, coal and tar is finely ground and made into a fluid paste by addition of water, and heated in revolving furnaces such as are used for cement (*see later*). A product containing 60 to 70 per cent. of barium sulphide soluble in water is thus obtained, and on addition of 1 to 2 per cent. of caustic soda (at 36° Bé.) the almost colourless sulphide crystallises from the concentrated liquid. The residue, insoluble in water, is dissolved in hydrochloric acid to obtain $BaCl_2$.

The preparation of the sulphide from the sulphate in the electric furnace was mentioned in dealing with barium oxide and hydroxide, the sulphide yielding hydroxide and hydrosulphide when treated with hot water. Barium sulphide fixes CO_2 and moisture from the air and undergoes oxidation. It is soluble in water and crystallises with $6H_2O$; it is phosphorescent in the dark. It is used for the preparation of various other barium salts (*see above*), and also replaces barium hydroxide in the treatment of beet-sugar molasses, because on treatment with 7 parts of hot water it is largely transformed into barium hydroxide, which partially separates in crystals on cooling. It is also used for the precipitation of arsenic from sulphuric acid to be used in electric accumulators, and is sometimes employed for vulcanising and weighting rubber. Commercial barium sulphide varies greatly in strength and should always be tested analytically. The crude sulphide costs £4 to £4 16*s.* per ton, and when purified £40.

Italy produced 14 tons in 1906, 1960 tons in 1907, 2260 tons in 1908, of the value of £7240, 1048 tons in 1910, 1188 in 1911, 995 in 1912, 1394 in 1913, 1982 in 1914, and 1920 in 1915.

BARIUM CARBONATE : $BaCO_3$. This compound exists as *witherite* in rhombic crystals, isomorphous with aragonite and strontianite, and has a specific gravity of 4·3. It abounds in England (Alstonmoore, Fallowfield), Styria, Siberia, Chili, and Sicily. The temperature of dissociation of barium carbonate in an atmosphere free from CO_2 is very high (1350°), and it is, therefore, not easy to obtain the oxide from the carbonate by heating it. In an atmosphere of CO_2 it half melts at 1350°, perhaps because a basic carbonate, $BaO,BaCO_3$, the melting-point of which would be 1454°, is formed. The thermal equation for the formation of barium carbonate is $BaO + CO_2 = BaCO_3 + 62{,}200$ cals. It may be obtained from the sulphide with CO_2 or from soluble barium salts with sodium carbonate.

According to Fr. Pat. 408,357 of 1909 and the supplementary patent of 1910, barium carbonate may be prepared by heating 100 parts of powdered barium sulphate with 250 parts of sodium carbonate and 200 parts of water in an autoclave at 5 atmospheres pressure. It is then filtered and decanted, yields of as much as 97 per cent. being finally obtained.

It forms a white substance insoluble in water and in alcohol and soluble in HCl, with which it forms $BaCl_2$. It is used in the manufacture of terra-cotta, glass, and enamels. Powdered witherite costs about £7 4*s.* per ton and the precipitated carbonate £8 to £12.

The Italian imports and exports were as follows (tons):

	1908	1909	1912	1913	1914	1915	1916	1917
Imports .	13·7	606	16·3	50	113·2	151·2	13·6	20
Exports .	32·4	—	—	—	10	137·6	284·5	133

The output was 300 tons in 1902, 650 in 1908, and 42 in 1910.

The United States imported witherite to the value of £5160 in 1912, part of this being added to clay to prevent the bricks from efflorescing.

In 1907 Germany exported 3750 tons of precipitated barium carbonate, in 1909 3400 tons, in 1910 5363 tons, and in 1911 8234 tons (£40,000).

France imported 1346 tons of natural barium carbonate in 1913, 442 in 1914, and 943 in 1915.

HYDRAZINE

Just as ammonia has a certain similarity to the alkali metals, so the divalent radical, N_2H_4 (Hydrazine, p. 376), has a certain similarity to the divalent alkaline earth metals, and yields a series of derivatives analogous in constitution and properties.

Thus **Hydrazine Sulphate**, N_2H_4,H_2SO_4, which is only slightly soluble in water, is known, and so is a chloride, $ClNH_3{\cdot}NH_3Cl$, etc. Certain properties of these compounds are similar to those of the alkali metals. Hydrazine also forms compounds with hydrazoic acid, etc.

MAGNESIUM SUB-GROUP

This comprises glucinum, Gl = 9·1; magnesium, Mg = 24·32; zinc, Zn = 65·37; cadmium, Cd = 112·4, and to a certain extent mercury, Hg = 200. The basicity of magnesium oxide constitutes a link with the alkaline earth metals which have just been described. The metals of this group, however, do not decompose water even on heating, and their oxides are either very slightly soluble or insoluble in water. The hydroxides and carbonates are less stable, and the chlorides are partially decomposed in presence of water into oxides and HCl. [*Translator's note.*—The statement that these metals do not decompose water is only true to a certain extent.] Another important difference between this group and that of the alkaline earth metals consists in the solubility of the sulphates. Zinc and magnesium sulphate crystallise with $7H_2O$ and form mixed isomorphous crystals with other sulphates.

Glucinum and magnesium are light metals (Gl, sp. gr. 1·8, Mg 1·74), whilst zinc, cadmium, and mercury are heavy metals (Zn = 7·1, Cd = 8·6).

The sulphides of the alkali and alkaline earth metals are soluble in water, whilst those of the heavy metals are insoluble in water and in dilute acids. The sulphides of magnesium and glucinum are not precipitated from solutions of their soluble salts by H_2S.

The closest similarity in this group exists between glucinum and magnesium, and the next closest between zinc and cadmium. Mercury is in many ways allied to zinc and cadmium in mercuric compounds, where it behaves as a divalent element, whilst mercurous compounds show a behaviour approaching that of certain derivatives of copper and silver.

MAGNESIUM: Mg, 24.32

This element is not found free in nature, but abounds in various minerals, especially as carbonate in *magnesite*, $MgCO_3$, and in the double carbonate of calcium and magnesium, *dolomite*, $MgCa(CO_3)_2$; it is also fairly widely diffused as a silicate, as *talc*,[1] which is an acid metasilicate, $Mg_3H_2(SiO_3)_4$; *asbestos*,[2] which is an anhydrous silicate; *serpentine*, $Mg_3H_2Si_2O_8,xH_2O$,

---

[1] Steatite is a greenish, reddish, or brown variety of talc, but gives a white powder; it is greasy to the touch, soft (hardness = 1), has density 2·6 to 2·8, and when heated strongly (to below 1500°) it becomes almost white and considerably harder, losing water and changing its form slightly. It is used as a solid lubricant, for making gas burners, for writing on glass, and as an electric insulator.

[2] **Asbestos** was known to the ancients, who used it in the form of fabrics as winding-sheets for corpses which were to be cremated, on account of its resistance to fire, by which means they were able to recover the pure ashes. In its chemical composition it is a magnesium silicate in which varying quantities of magnesia are replaced by lime, together with ferrous oxide and alumina as impurities. It belongs to the group of the *amphiboles*. Its composition varies with the source from which it is obtained; thus, for example, Canadian asbestos (*chrysotile*) consists of hydrated magnesium silicate mixed with 2 to 6 per cent. of ferrous oxide, whilst that from the Cape contains less magnesia and more iron oxide. It has a more or less pronouncedly fibrous structure.

The most important deposits are found in Canada, then in Russia, the Cape of Good Hope, which is a hydrated disilicate; *meerschaum*, $Mg_2Si_3O_8,2H_2O$, but most abundantly in the form of magnesium salts in the Stassfurt deposits (*see* p. 529), as *Carnallite*, *Kieserite* ($MgSO_4,H_2O$), *Kainit*, *Schönite* ($K_2SO_4,MgSO_4,6H_2O$), etc. It also abounds in sea water in the form of chloride and sulphate. The Dead Sea contains about 10 per cent. of $MgCl_2$.

Metallic magnesium was at one time prepared by reducing the chloride, $MgCl_2$, with metallic sodium (Davy's process, modified by Bassy in 1830); to-day, however, it is all prepared electrolytically in the Hemelingen works at Bremen and a small amount in the Elektron works at Griesheim, by the electrolysis of molten magnesium chloride, as was proposed by Bunsen in 1852, or preferably from molten carnallite ($MgCl_2,KCl$) which is more easily obtained free from water.

The operation is conducted in a steel crucible, which acts as a cathode, the anode being formed of carbon. During the fusion and electrolysis of the carnallite, potassium and sodium chlorides are added in such proportions that the molten mass always contains 41·6 per cent. of $MgCl_2$, 32·6 per cent. of KCl, and 25·66 per cent. of NaCl, thus forming a kind of artificial carnallite. A current of 100 amps. per square metre at an E.M.F. of 7 to 8 volts is used. The magnesium collects in numerous small spheres, which are separated by crushing the mass after cooling. These magnesium spheres are melted together in a crucible with or without the addition of fluxes (CaF_2), and are then cast into bars. According to U.S. Pat. 935,796 of 1909, magnesium is prepared electrolytically by first forming an alloy of aluminium and magnesium.

Magnesium is a metal of silvery appearance which does not alter in dry air. Its specific gravity is 1·7; it is ductile and malleable and when heated may be drawn into wires and thin ribbons. It melts between 750° and 800° and distils at about 1100°. It is resistant to the action of alkalis and is easily dissolved by dilute acids with evolution of hydrogen. It conducts the electric current like aluminium, and heat somewhat better (about half as well as copper). When heated in a gas flame it catches fire and burns with a very bright light,

---

and a little in the United States and Italy. It is dislodged from the rock and fibrous blocks are liberated which are crushed with suitable machinery in order to separate them from dust and also to separate the long from the short fibres. Asbestos is found in Italy in the Val Malenco and Piedmont (Val d'Ossola and Val di Lanzo), and the deposits are exploited by English firms. Italian asbestos is inferior to the Canadian product, as its fibres are shorter. Italy's production, imports, and exports were as follows (tons):

	1908	1910	1912	1913	1914	1915	1916	1917
Production .	360	175	169	175	171	163	—	—
Imports .	2550	2051	4226	4570	2710	5380	5428	3728
Exports .	193	485	571	672	508	148	258	165

The crude asbestos produced in Italy is valued at about £20 to £22 per ton and the imported product at £24.

The United States produced 930 tons of asbestos in 1908, 3000 in 1909, 7000 in 1911, and 4000 in 1912, and the imports of raw asbestos were 52,800 tons in 1910 and 62,400 (£288,800) in 1911.

Canada produced 380 tons in 1880, 66,000 in 1908, 63,000 (£400,000) in 1909, and 80,000 in 1912 (65,000 tons exported to the United States). The industry in Canada employs 2000 workpeople, the capital invested in it being £4,800,000. In the Black Lake district (Quebec) the reserve of asbestos rock is estimated at 45,000,000 tons.

England imported 11,566 tons in 1909 and 14,438 (£114,000) in 1910.

Russia produced 9356 tons in 1907, and in 1913 16,900 tons were produced in the Urals.

Cape Colony produced 550 tons in 1907.

The following varieties are distinguished commercially according to the varying length of the fibres: Crude, first quality; crude, second quality; fibre; paper stock, and asbestine. It has a specific gravity of 2·5 to 2·9, is resistant to the action of acids and fairly resistant to that of dilute alkalis.

It is used for insulating covers for boilers, for hangings and curtains, as cardboard for lining boiler tubes, joints, etc., by mixing to a paste with sodium silicate, and so on. Incombustible cardboard and paper are also prepared from it. When mixed with cement to a paste it forms *eternite*, which is used in large sheets for covering roofs, etc. (6 parts of cement to 1 part of asbestos).

The price varies with the length of the fibre from £2 (asbestos powder) to £80 per ton when the fibre is long.

Asbestos thread costs up to 2*s*. 5*d*. per kilo, cord 2*s*. 9*d*., and board 7½*d*.

producing powdery, white magnesium oxide. The magnesium light is very rich in chemically active rays and is, therefore, used for photographic purposes. Fine magnesium powder, when projected into a gas flame, gives an extremely luminous light, and in photography magnesium flash-lights are used which consist of 1 part of potassium chlorate and 2 parts of magnesium powder, or better, of equal parts of magnesium powder and thorium nitrate. It does not decompose water in the cold, but evolves hydrogen abundantly at 100°.

Magnesium reduces many oxides, liberating the corresponding metals or non-metals, such as boron, carbon, silicon, etc. The demand for magnesium is relatively small, as it is only used for photographic illumination, for lanterns, and for fireworks. Some magnesium is now used for the preparation of a very interesting alloy, containing 10 to 20 per cent. of Mg with 80 to 90 per cent. aluminium, called **Magnalium** (*see* Aluminium). When added to brass or copper, it prevents blow-holes, and it is now frequently used for the purification of various alloys in the fused state; thus, aluminium is purified by addition of 2 per cent. of magnesium, of which about 1·5 per cent. is retained, this giving the aluminium double the tensile strength and four times the resistance to shock or vibration, besides rendering possible clean cutting, ready polishing, and more easy mechanical working.

The world's consumption of magnesium in 1899 appears not to have exceeded 12 tons, but it is now increasing; indeed, the United States alone in 1913 imported (from Germany) at least 17 tons, and prior to the European War the world's consumption approached 100 tons.

The price was £20 per kilo in 1870, but after the electrolytic manufacture was started in 1884 it fell rapidly, and in 1902 was 16*s.* per kilo for bars, 32*s.* for wire or ribbon, and 14*s.* for powder; in 1914 bars cost less than 8*s.* per kilo. During the European War the price rose rapidly in all countries, and in the United States, where the manufacture was immediately started, it reached 22*s.*, then 48*s.*, 64*s.*, and even 80*s.* per kilo.; in 1916 it fell to 52*s.*

MAGNESIUM OXIDE: MgO (BURNT MAGNESIA)

This compound is obtained on heating the carbonate, $MgCO_3$, to redness, and according to the temperature to which it was heated the product is more or less light. It is ordinarily obtained as a soft and very white powder by heating basic magnesium carbonate (magnesia alba, *see below*) in stoneware crucibles to a moderately high temperature (dark red) until it no longer effervesces with HCl. In order to obtain heavy burnt magnesia, the magnesia alba is well compressed in crucibles and heated to a white heat. The highest degree of compactness is obtained by heating to redness the magnesium carbonate obtained by precipitating a boiling solution of magnesium sulphate with sodium carbonate, boiling for some time, washing the precipitate, and drying it. This magnesia is also very pure.

It is obtained at Neustassfurt from $MgCl_2$ as a secondary product in the preparation of chlorine (p. 156). Its heat of formation is 143,900 cals. It is almost completely insoluble in water, and melts at the temperature of the electric furnace with partial evaporation (when pure it melts at 2800°).

Magnesia is used in medicine and also as a refractory and infusible material for furnaces which are required to withstand the highest temperatures, because it is not reduced by carbon even at the highest temperatures known.[1] Bricks

---

[1] In Italy, for the basic lining of Siemens-Martin furnaces, calcined natural magnesia specially imported from Styria is used, which contains about 85 per cent. of magnesium oxide, 2 per cent. of calcium oxide, 8 per cent. of iron oxide, and 2 per cent. of silica. This product is more suitable than that from Eubœa in Greece, which contains 94 to 96 per cent. of MgO, 1·25 to 2·9 per cent. of CaO, 0·06 to 0·26 per cent. of Fe_2O_3, 0·16 to 0·42 per cent. of Al_2O_3, and 0·50 to 3·15 per cent. of SiO_2. This contains little or no iron, and does not, therefore, form in the furnace magnesium ferrites, which increase the stability and permanence of the lining. The *giobertite* deposits of Piedmont contain very much silica (25 to 26 per cent. of SiO_2), and give a very fusible lining, but this product is more suitable for the ceramic industry.

In 1908 Italy imported 12,000 tons of semi-fused calcined magnesite for ceramic and metallurgical purposes.

of molten magnesium oxide are to-day prepared for lining electric furnaces. They are produced in electrical furnaces and are then poured into moulds to cool.

Nernst constructed his incandescent electric lamp by utilising the property of magnesium oxide and other oxides of the rare earths (zirconia, yttria, etc., p. 504) of becoming conductors of electricity when heated. The filament or small cylinder of metallic oxide present in the lamp is first heated by means of an electrical resistance, and allows the current to pass when it has acquired a certain temperature, so that the oxide then becomes incandescent, emitting a very intense light. The use of this Nernst lamp has gradually established itself, and a powerful company has recently been formed in America for preparing it on a very large scale. In Europe these lamps are already widely used and consume 1–2 watts per candle-power, but after 500 hours their luminosity diminishes by 20 per cent., whilst the consumption of energy rises to 1–7 watts.

Heavy calcined magnesia costs £48 per ton, whilst the light product costs about £56.

Impure calcined magnesia was imported into, and exported from, Italy as follows (tons):

	1908	1910	1912	1913	1914	1915	1916	1917
Imports .	14	616	1247	1316	1224	807	182	24
Exports .	27	215	1062	1031	1455	1072	395	483

Further, Italy exported 96 tons of pure calcined magnesia in 1910, 193 in 1912, 219 in 1913, 246 in 1914, 318 in 1915, 256 in 1916, and 347 (£48,920) in 1917.

MAGNESIUM PEROXIDE : MgO_2. This is obtained in an impure condition from sodium or barium peroxide with magnesium sulphate or chloride in concentrated solution.

It is used to some extent in the bleaching of woollen and silken fabrics, because the bath has a less energetic alkaline reaction, although very costly (16*s.* per kilo). A product called "novozon," containing magnesium dioxide, has been introduced medicinally as an energetic antiseptic. Its commercial value depends on its active oxygen content.

MAGNESIUM HYDROXIDE : $Mg(OH)_2$. If sodium hydroxide is added to a solution of a magnesium salt $Mg(OH)_2$ is precipitated, which is only slightly soluble in water and still less (1 : 50,000) if an excess of the precipitating agent (NaOH) is present. It imparts an alkaline reaction to water and is able to fix CO_2 from the air.

Aqueous solutions of ammonia and of ammonium salts completely dissolve magnesium hydroxide, because the $NH_4^{\cdot}$ ions of these salts unite with a few OH' ions, which the hydroxide $Mg(OH)_2$ liberates in solution, and form soluble ammonia or $NH_3 + H_2O$; as these OH' ions react, others are detached from the magnesium hydroxide, and thus the reaction continues until the whole of the hydroxide has dissolved (p. 102). Thus magnesium salts in general are not precipitated by the common reagents for the other heavy metals when ammonia and ammonium salts (NH_4Cl) are present. When heated, magnesium hydroxide loses water, forming MgO.

MAGNESIUM CHLORIDE : $MgCl_2$. This compound is obtained in large quantity from the mother-liquors of the Stassfurt salts which contain $MgCl_2$, $MgBr_2$, and $MgSO_4$.[1] These are evaporated in open iron pans to 42° Bé. The

---

[1] Reference has already been made (p. 532) to the serious problem presented by the disposal of the waste liquors from the treatment of Stassfurt salts. The percentage composition of these liquors is approximately: NaCl, 0·95; KCl, 1·25; $MgBr_2$, 0·30; $MgSO_4$, 2·22; $MgCl_2$, 29·50, and H_2O, 65·78. They are too abundant to be treated for the extraction of $MgCl_2$, and owing to the damage they cause in rivers, the proposal has been made to construct a canal about 100 kilometres long to carry them to the sea, but this would cost at least £1,000,000. Evaporation is too troublesome, and the use of the liquors for watering town and country roadways has been suggested; trials in this direction appear to have given encouraging results, although in some districts a troublesome mud has been formed on the roads. A certain amount may be used for making articles of Sorel cement (*see above*), but very careful working is necessary to voiad failure.

salts which are first precipitated are separated and the concentrated solution is then allowed to cool, when it sets to a radiating crystalline mass of $MgCl_2$, $6H_2O$. If the concentration is carried up to 45° Bé. molten $MgCl_2$ is obtained, but in order to obtain 80 per cent. $MgCl_2$ without decomposition and formation of HCl it is necessary to heat in a vacuum up to 175°. When a solution of $MgCl_2$ is evaporated and the residue heated at 106° or a higher temperature, not soluble anhydrous $MgCl_2$, but almost insoluble basic magnesium chloride is obtained, HCl being liberated: $2MgCl_2 + H_2O = 2HCl + MgCl_2, MgO$.

Magnesium chloride volatilises at a red heat and partially decomposes in presence of minimal quantities of water, forming HCl and magnesium oxychloride, $MgCl \cdot OH$. Even in hot aqueous solution it forms HCl at 175°, and for this reason water containing much magnesium chloride, and especially sea water, should not be used in steam boilers. Magnesium chloride has a bitter taste and is very hygroscopic.

It is used for the preparation of HCl and as a dressing for cotton and woollen textiles. Much $MgCl_2$ is also used in the preparation of *lignolite*, *xylolite*, or *magnesia cement*, which is a very hard mixture formed of a paste containing sawdust, magnesium chloride, and magnesium oxide in suitable proportions. It is also called *Sorel cement* from the name of its discoverer (1867). Its composition varies between $MgCl_2,5MgO,13H_2O$ at the commencement of the reaction, and $MgCl_2,2MgO,9H_2O$ at the end of the reaction after the paste has been made up for some days. A cement of this character may be produced as follows: 100 parts of magnesia (a very soft oxide freshly heated to redness) + 300 parts or less of infusorial earth or sawdust, both of which are made to a paste with about 713 parts of a concentrated solution (32 per cent.) of magnesium chloride. These ingredients must be mixed continuously for several hours, sometimes even for more than a day, so that the mass sets almost to a jelly without separation of the components. The maximum hardness is acquired only after exposure to the air for two or three weeks. Sbertoli (Ger. Pat. 221,641 of 1908) mixes $MgCl_2$ and MgO in equimolecular proportions, dries this mixture and thus obtains a powder which is placed on the market as such, and is used in a similar manner to Portland cement.

Lignolite is used for flooring, walls, and various decorations. A magnesium chloride ammonia, $MgCl_2,NH_3$, which is of great use in soldering metals, is obtained by heating a mixture of 883 grams of anhydrous magnesium chloride, dissolved in a little water, with 650 c.c. of ammonia of 22° Bé. until the mass becomes clear. After cooling, it becomes solid and is kept in a dry place. In use it is rubbed over the metals at the points to be soldered before they are heated.

The crude fused chloride costs about £4 per ton and the refined anhydrous product £20. In 1904 Italy imported 480 tons, of the value of £1540, in 1909 1452 tons, of the value of £5228, in 1912 1387 tons, in 1913 1565 tons, in 1914 1343 tons, in 1915 293 tons, in 1916 55 tons, and in 1917 59 tons. Germany exported 21,862 tons in 1905, at about £2 per ton, in 1908 it produced 30,000 tons, of the value of £28,000, and in 1912 it exported 39,100 tons (including a little calcium chloride).

MAGNESIUM SULPHATE : $MgSO_4$. This salt commonly crystallises with $7H_2O$ in colourless rhombic prisms and then forms so-called *Epsom salts*, which lose $6H_2O$ at a temperature of 150° and the remainder at 200°. It is very soluble in water (1 : 2 in the cold and 1 : 1 on heating), and crystallises from concentrated solutions at 30° with $6H_2O$, but in another crystalline form.

It abounds at Stassfurt in the form of schönite, $MgSO_4,K_2SO_4,6H_2O$, of kieserite, $MgSO_4,H_2O$, and of kainit.[1] On concentrating solutions of these salts, $MgSO_4,H_2O$ separates because it is less soluble than the chlorides; it is purified by recrystallisation from water and then forms $MgSO_4,7H_2O$, which is isomorphous with various other sulphates, such as $NiSO_4,7H_2O$ and $ZnSO_4$,

---

[1] Kainit (*see* pp. 530, 532, 543) was thought to have as its principal component potassium sulphate (about 35 per cent.) together with magnesium sulphate and chloride, but, from van't Hoff's studies it appears that the potassium occurs in kainit as the chloride (about 23 per cent.), together with magnesium sulphate, etc.

$7H_2O$; it forms mixed crystals with ferrous sulphate, $FeSO_4,7H_2O$, and cobalt sulphate, $CoSO_4,7H_2O$, forming rhombic or monoclinic crystals according to the preponderance of the one or the other (isodimorphism, p. 116). Numerous double salts, isomorphous with one another, are also known, and are obtained from all these sulphates by addition of potassium or ammonium sulphate; all of these have the formula, $X_2SO_4,MeSO_4,6H_2O$, where X represents K or NH_4, and Me may be Mg, Fe, Ni, Co, Zn, Cu, etc.; thus we have $K_2SO_4,MgSO_4,6H_2O$.

Magnesium sulphate also crystallises with quantities of water varying from 1 to 12 mols. It is used in the preparation of K_2SO_4 and $BaSO_4$, for finishing cotton fabrics, and for weighting silk and paper. It is also frequently used in medicine, and has been proposed as a fertiliser in certain cases. The pure crystallised commercial sulphate costs £2 16*s.* to £3 4*s.* per ton, and when anhydrous £10 per ton. In Italy 1100 tons of magnesium sulphate were produced in 1893, subsequent statistics being as follows (tons):

	1905	1908	1910	1912	1913	1914	1915	1916	1917
Production .	1880	2380	2520	2717	2257	2871	3246	—	—
Imports .	114	304	419	794	509	432	63	1	—
Exports .	—	10	27	10	18	9	25	103	164

Germany produced 58,567 tons in 1905 and exported 22,200 tons in 1912.

MAGNESIUM CARBONATE : $MgCO_3$. This compound is found in nature in the form of *magnesite* or *giobertite*, $MgCO_3$, especially in Austria (Silesia, Styria, and Moravia), Macedonia, Norway (Snarum), United States (California), India, Transvaal, and Canada, but the best quality is that from the Island of Eubœa[1] or, in Italy, that from Val di Susa (Caselette) and Elba; recently it has been discovered in a purer form at Castiglioncello (Leghorn). Magnesite (compact, amorphous, or crystalline) is attacked slowly by hydrochloric acid and is dissolved more rapidly in sulphuric acid (difference from dolomite); it is infusible in the blowpipe flame.

It is widely diffused as *dolomite*, $MgCO_3,CaCO_3$. The lime is separated from the latter in the following manner: The calcined dolomite is finely powdered and suspended in water which is then saturated with CO_2; the magnesia dissolves before the lime, forming the bicarbonate, $Mg(HCO_3)_2$, which loses CO_2 and H_2O on heating, forming $MgCO_3$.

According to Fr. Pats. 413,793 and 454,162 (1913), only the theoretical quantity of CO_2 is consumed if this acts under pressure; when the filtered solution is cooled to 10° to 15° in closed vessels, the hydrated carbonate, $MgCO_3,5H_2O$, crystallises out, whereas in open vessels, $MgCO_3,3H_2O$, which is stable even at 40°, separates.

Magnesium carbonate is obtained by precipitating a soluble magnesium salt with sodium carbonate or by heating MgO with sodium bicarbonate, although the white mass obtained is a basic carbonate, called *magnesia alba*, $Mg(OH)_2,4MgCO_3,5H_2O$, which on heating with water in presence of CO_2 forms $MgCO_3,3H_2O$. Double salts are also known, such as $MgCO_3,K_2CO_3,4H_2O$.

---

[1] The compositions of certain commercial magnesites are as follows. If used for refractory materials they should be almost free from silica and lime. The purer forms are used as chemical products, and that used for earthenware should contain very little iron (Elba):

	Island of Eubœa	Silesia	Elba and Caselette
MgO . . .	46·93 %	44·06 %	32 – 42 %
CO_2 . . .	51·67	48·10	36 – 46
$Fe_2O_3 + Al_2O_3$.	0·58	0·32	trace – 1
SiO_2 . . .	0·20	5·02	8 – 16
CaO . . .	0·42	1·26	1 – 3·5
H_2O . . .	0·20	1·24	—

Silesian magnesite sometimes contains layers of organic substances which, when heated, yield products contaminating the carbon dioxide.

Magnesium carbonate begins to dissociate at 500°, forming MgO and CO_2, and at 620° decomposes instantly. It is, in fact, used for obtaining CO_2 and magnesium oxide employed in the manufacture of refractory materials and the bases for Martin-Siemens and electric furnaces. To economise in transport cost and to enrich the magnesite in MgO it is, besides being cleaned at the quarries, also calcined there in lime kilns or revolving furnaces until only 1 to 2 per cent. of CO_2 remains.

USES. Pure magnesium carbonate is used in medicine and as a powder for cleaning the teeth, metals, etc.; it is also incorporated in various colours for paints.

STATISTICS. Germany imported 69,064 tons of magnesite in 1912. Austria exported 114,000 tons (especially from Styria) in 1907, and England produced 18,000 tons in 1907. From the island of Eubœa 56,000 tons were exported in 1907. The United States produced 8000 tons in 1908 and imported 120,000 tons (£200,000) in 1911. India produced 2600 tons in 1905, but scarcely any since then.

Italy produced 910 tons of giobertite in 1910 and 600 tons in 1913; also about 450 tons per annum of artificial magnesium carbonate, about one-half being exported. In 1910 Italy imported 11,000 tons of magnesite from Eubœa and Styria at 16*s*. to 18*s*. per ton.

MAGNESIUM PHOSPHATES. The primary phosphate is not known and the tertiary phosphate, $Mg_3(PO_4)_2$, is of little importance. The secondary phosphate, $MgHPO_4,7H_2O$, is more commonly obtained in a crystalline form by precipitating a soluble magnesium salt with secondary sodium phosphate, Na_2HPO_4, but in presence of ammonia and ammonium salts, magnesium ammonium phosphate, $MgNH_4PO_4,6H_2O$, is precipitated, which is very insoluble, and is therefore used in the quantitative separation of magnesium from solutions of its salts. On heating to redness it forms magnesium pyrophosphate, $Mg_2P_2O_7$. Magnesium ammonium phosphate is present in guano and urine, and often forms bladder-stones.

MAGNESIUM SILICATES. Numerous silicates of magnesium are found as minerals which have already been mentioned (p. 668), and a gelatinous silicate, $3MgSiO_3,5H_2O$, is produced artificially by precipitating a soluble magnesium salt with sodium silicate, and is used for decolorising vegetable and mineral oils. The so-called *fullers' earth* is also imported into Europe for this purpose (*see* Aluminium Silicate).

TALC is a hydrated magnesium silicate, $Mg_3H_2Si_4O_{12}$, which is found in various countries stratified in compact masses, varying in colour (white, green, brown, pink), structure (opaque with earthy fracture or in translucent, nacreous, flexible but non-elastic lamellæ), and hardness (1 to 1·5 on Mohs' scale; it can be scratched with the nail); its density is about 2·6.

When it has a slightly fibrous structure and is translucent it constitutes steatite or soapstone, which is greenish or brownish-red, and gives a white, greasy powder. When heated, it hardens and loses water, but does not melt; it is almost unattackable by acids.

An artificial talc is obtained by treating with sodium silicate the solution of a magnesium salt, and washing and drying the precipitate formed.

Steatite is used as an insulator in electro-technics and for making jets for gas and acetylene. It is also used as a lubricant and for softening gloves, shoes and rubber, for making tailors' chalk and slate pencils, and for removing grease spots from cloth.

Powdered talc is used in making sealing-wax, pasteboard, carpets, pigments, face paints, rubber, etc.

The output of talc in the United States was 96,600 tons in 1905, 107,000 (£280,000) in 1908, and 135,000 in 1910. In Italy the production of ground talc was 6490 tons in 1905, 10,930 (£13,312) in 1908, and 13,343 in 1910, this coming mostly from the Pinerolo district at about 24*s*. to 40*s*. per ton in lumps at the quarry or 64*s*. to 72*s*. in natural powder. The output was 16,240 tons in 1912, 24,001 in 1913, 22,478 in 1914, 21,942 (£64,070) in 1915, and 25,933 in 1916.

France exported 11,497 tons of powdered talc in 1913, 8752 in 1914, and 7574 in 1915.

MAGNESIUM NITRATE: $Mg(NO_3)_2,6H_2O$. This is obtained by neutralising MgO with HNO_3, and then evaporating until crystallisation occurs. It is a hygroscopic salt, soluble in both water and alcohol, and is used for strengthening incandescent mantles at the point of suspension.

MAGNESIUM NITRIDE : Mg_3N_2. This is obtained as a yellowish porous mass on heating magnesium in an atmosphere of nitrogen or in a current of ammonia :

$$Mg_3 + 2NH_3 = Mg_3N_2 + 3H_2.$$

When poured into water it becomes heated and ammonia is evolved. When heated with soda and carbon it gives sodium cyanide: $Mg_3N_2 + Na_2CO_3 + C = 2NaCN + 3MgO$; after being started, the reaction is exothermic. The same result is obtained directly when $Mg + C + Na_2CO_3$ are heated in presence of nitrogen.

GLUCINUM: Gl, 9.1

This element is also known as **Beryllium.** It is called glucinum on account of the sweet taste of its salts. It occupies a position in the group of divalent metals analogous to that of lithium in the alkali metal group. Thus it has the least atomic weight, and like lithium, which tends in its chemical properties to depart from those of its group, approximating to magnesium, glucinum is similar to aluminium in many of its derivatives; thus it is only slightly attacked by HNO_3 and dissolves in alkali hydroxides with evolution of H.

Glucinum is very rare and is found in *emerald* and in *beryl*, which is a double silicate, $Al_3Gl_3(SiO_3)_6$, and also in *chrysoberyl*, which is a glucinum aluminate, $GlAl_2O_4$. On decomposing glucinum with K_2CO_3 and then separating the silica with H_2SO_4, a solution of alum and of glucinum sulphate remains, from which alum first crystallises, the iron and aluminium present as impurities being separated with ammonium carbonate. The mother-liquors which contain the glucinum salt are acidified with HCl, and glucinum hydroxide then precipitated with NH_3. The hydroxide may then be used for the preparation of all the other salts.

Metallic glucinum is obtained by melting the double fluoride, $GlF_2,2KF$, with metallic sodium. It is a white, ductile metal of sp. gr. 1·64, soluble in acids and in dilute alkalis, but not in dilute HNO_3. It does not alter in the air and does not decompose water even at 1000°. It melts at 1800°.

Crystallised glucinum is one of the most expensive rare metals and costs £2 per gram.

GLUCINUM OXIDE : GlO, is obtained by heating the hydroxide. When the oxide has been strongly heated to redness it dissolves in acids with difficulty (similarly to Al_2O_3).

GLUCINUM HYDROXIDE : $Gl(OH)_2$. This compound is obtained in a gelatinous form by precipitating a soluble glucinum salt with NH_3 (in a similar manner to Al) and dissolves in ammonium carbonate or in sodium hydroxide solution. It separates from these solutions on prolonged boiling.

GLUCINUM CHLORIDE : $GlCl_2,4H_2O$. This compound is obtained on heating GlO with carbon in a current of chlorine, similarly to $AlCl_3$. It sublimes easily, and the atomic weight of glucinum may be deduced from its vapour density.

GLUCINUM CARBONATE : $GlCO_3$. This is soluble in H_2O and readily evolves carbon dioxide.

GLUCINUM SULPHATE: $GlSO_4$. This compound crystallises from water with 4 or $7H_2O$, according to the temperature. It still retains $2H_2O$ at 105° and becomes anhydrous at 260°.

Glucinum salts cost £4 to £6 per kilo.

ZINC: Zn, 65.37

Zinc is found abundantly in nature as *Blende*, ZnS, and as *Calamine* or *Smithsonite*, $ZnCO_3$, minerals which are often found together with lead ores, and are smelted in Belgium, Silesia, England, Poland, North America, and

Sardinia. The deposits of Lombardy, Piedmont, and Belluno are less important.[1] Almost 70 per cent. of the Italian mineral is calamine.

The manufacture of zinc was started at Bristol in 1743, and then extended in the year 1807 to Liége, and later acquired great importance in Silesia. As early as the thirteenth century zinc was worked by the Indians and later by the Chinese. The largest works are now in Belgium, Germany, and the United States.

The object of the primary treatment of the ores is to obtain zinc oxide, because metallic zinc is then easily obtained from the latter. The operation is simple in cases when zinc carbonate is being treated, because it is then sufficient to heat in reverberatory furnaces in order to separate the CO_2. The treatment of blende, on the other hand, presents many difficulties, so that it was only about thirty years ago, after repeated attempts, that a profitable smelting process was successfully carried out by employing suitable furnaces which allow of the utilisation of all the sulphur dioxide evolved and its conversion into sulphuric acid.

The poor zinc ores (20 to 25 per cent. Zn) abounding in nature cannot well be treated directly, so that they are first screened and enriched by ingenious mechanical devices to raise the zinc content to at least 35 to 40 per cent. (theoretical for $ZnS = 67$ per cent.).

Sulphide ores should be completely desulphured to extract all the zinc, and this is effected —more easily with rich than poor ores—in blende furnaces (p. 295), since even if zinc sulphate is formed this is decomposed above 900° into ZnO and SO_2; blende containing lead and lime is not readily desulphured. Ores with a basis of zinc carbonate or silicate are, however, torrefied in furnaces like lime-kilns in layers alternating with layers of coal (*see* p. 616), a white heat being avoided so that the metal may not be reduced.

The residual roasted ore is now heated with coal to 1200° to 1300° to reduce the zinc oxide to metal, and as the latter vaporises at 930° and the vapour is easily oxidised (even by steam or CO_2—the reaction being reversible), the zinc should be liberated in closed retorts with excess of coal (50 to 60 per cent. of small coke), so as to have always an atmosphere of carbonic oxide alone. The condensation of the metal distilling over demands care, since if the temperature in the condensers is too low, the metal condenses as dust, whereas if it is above 420°, zinc homogeneously melted collects; above 550° to 600°, many zinc vapours do not condense. If the zinc vapour is very highly diluted with gas, zinc dust separates in preponderance even above 420°.

In order to obtain zinc from the residues, which contain oxide mixed with other impurities, there are two separate processes, the Belgian and Silesian processes. In the former the powdered mass is mixed with coal (2 : 1), and distilled in numerous slightly conical clay retorts with a somewhat elliptical section, closed at the smaller extremity. The retorts are 1·2 to 1·4 metre long, about 30 cm. in vertical and 25 cm. in horizontal diameter, and are placed in the furnace in four or five superposed pairs, each sloping slightly downwards towards the front. Every furnace takes 150 retorts (in America up to 700), which form two opposite batteries (Fig. 263). To the open mouth of each retort, *a*, is fitted a small earthenware mouthpiece, *b*, into which the molten zinc flows and to the outer end of which is fixed a sheet-iron cylinder, *c*, about 1 metre long and 20 cm. in diameter, with a horizontal septum forming two long chambers and compelling the zinc vapour to condense

---

[1] Germany produced 731,000 tons of zinc minerals in 1905, 706,000 in 1907, and about 720,000 in 1910.

Silesia in 1910 had 280 old furnaces with 11,000 muffles and 175 multiple-hearth furnaces with 18,300 muffles. France in 1913 exported 58,203 tons of zinc ores, in 1914 21,278 and in 1915 5599; the imports were 178,720 tons in 1913, 99,124 in 1914, and 49,398 in 1915. The United States produces more zinc minerals than all other countries. England in 1913 produced 17,294 tons of zinc ores and 15,419 (£56,640) in 1914; in 1909 the imports were 73,800 tons and in 1910 92,572 tons; in 1910 121,117 tons of zinc were imported, in 1911 115,228 tons.

Italy's production and exportation (nine-tenths from Sardinia, with a mean zinc content of 40 per cent. Zn), are as follows (tons):

	1909	1910	1911	1912	1913	1914	1915	1916
Production .	—	146,607	140,269	150,076	158,782	145,914	80,622	94,043
Exportation .	123,936	127,315	133,471	152,840	144,644	89,776	59,734	80,180

as zinc dust (mixed with 4 to 8 per cent. ZnO and a little cadmium); the latter may be either sold (*see later*) or redistilled with fresh ore.

The furnaces are heated with gas which is obtained from suitable producers and is burnt with hot air from the heat-recovery chambers, *R* and R_1 (*see* Glass Furnaces, p. 634). When the retorts reach a certain temperature, reduction of the zinc oxide occurs with evolution of carbon monoxide, which burns with a pale flame; when, however, zinc vapour is liberated, the flame becomes luminous. At intervals of two or three hours the condensed molten zinc is removed from the mouthpieces with iron spoons and poured into moulds. Small retorts have to be used and charged only to the extent of one-half, since the mixture to be heated is a bad conductor of heat, and with large masses the interior would not attain the desired temperature. The roasted ore is mixed with a large excess of coal (up to 50 per cent. of the ore) so as to obtain a pulverulent residue in the retort; with little coal, the final residue would fuse and run down the retort and perforate it. In any case, the retorts do not usually last very long, the average life being 15 to 18 days in some works, although in others it is 25 or even 35 to 40 days. The retorts are very carefully prepared by mixing clay intimately with 15 to 20 per cent. of burnt clay, 10 to 15 per cent. of powdered chamotte (old broken retorts), and 5 to 10 per cent. of finely powdered coke or graphite (these additions are made to give a mass with a very small coefficient of expansion and thus capable of withstanding sudden changes of temperature). A good clay for these retorts should contain little iron, lime or alkali and not too much silica where highly basic ores (rich in lime and magnesia) are treated, or too much silica where acid ores (rich in silica) are treated. Such clay has a percentage composition approximating to: Al_2O_3, 34 to 38; SiO_2, 42 to 50; CaO, 0·5 to 1·5; MgO, 0·3 to 0·6; Fe_2O_3, 1 to 2; K_2O, 0·4 to 0·8; loss on calcination (CO_2 from carbonates, etc.), 12 to 17. The clay is powdered, mixed well with water, and allowed to ferment (as in the porcelain industry: *see later*) to render it more plastic, the remaining ingredients, together with 7 to 8 per cent. of water, being then intimately mixed in by means of a mixer; cylindrical blocks of it are then placed in a mould and a mandrel forced into the middle of the block by means of a hydraulic press, this enlarging the cavity to the desired diameter under a pressure of 200 to 300 atmos.

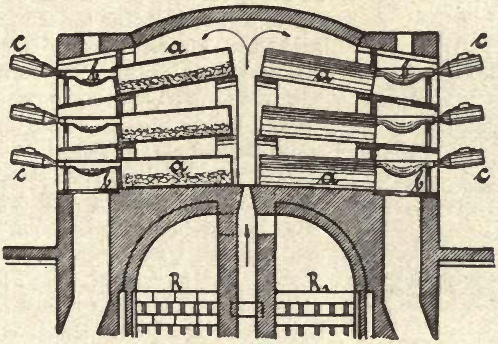


FIG. 263.

The retorts thus prepared are allowed to dry in the air for 10 to 15 days, then gradually in ovens at 40° to 50° for some days, at 60° to 75° for several days longer, and then in furnaces heated by the waste gases from the zinc furnaces; they are thus brought slowly to 900° to 1000°, and are then either introduced while hot into the zinc furnace or allowed to cool gradually in ovens at successively lower temperatures.

At the completion of the distillation and after removal of the mouthpieces, the powdery residue left is extracted from the retort by iron ladles. The whole mass falls into iron trucks, and when cold is lixiviated with water to remove the coal, the residue—which contains lead and 4 to 6 per cent. of the original zinc—passing to the lead works, where the zinc and lead are recovered.

The mouthpieces containing the zinc dust (3 to 4 per cent. of the total zinc of the ore) are placed upright and stoppered as soon as they are detached and while still hot, as otherwise the zinc dust would oxidise and ignite in the air.

Hegeler has recently made a marked improvement in the Siemens furnace used in Belgium, more regular and uniform heating of all the retorts being attained with a consumption of 3 tons of coal for heating and 1 ton of coal for reduction per ton of crude zinc produced.[1] Good results have also been obtained with vertical retorts.

By the Silesian system poor ores can also be treated. A mixture of powdered ore and coal is placed in a large number of muffles arranged in a double row in a furnace (Fig. 264). The muffles have an elbow-shaped delivery tube at the upper part of the outer end, which passes into a common chamber where all the molten zinc and zinc dust is collected.

Both the Belgian and Silesian processes require large amounts of coal (up to eight times the weight of the zinc obtained), and the loss of zinc is always more than 15 per cent. and may even be 20 to 25 per cent., since some zinc remains in the retorts with the distillation residue, part of the zinc escapes through the unavoidable cracks and pores of the retorts, and part of the zinc vapour burns during the discharge of the retorts; further, some zinc combines in the hot with the materials of the retorts, forming blue zinc aluminates.

The loss is greatest with poor ores (15 to 20 per cent. Zn) and least with rich ores (30 per cent. or more). Numerous and costly attempts to work zinc ores continuously (as is done with iron in blast furnaces) and to diminish losses have not led to any good results, much zinc dust, some oxide, and little molten zinc being obtained.

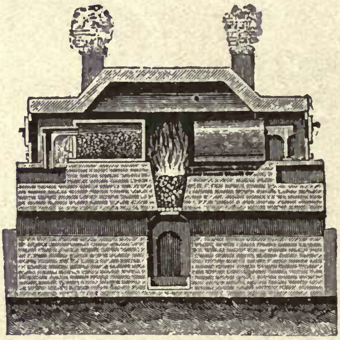


FIG. 264.

In 1840 the losses in the Vieille Montagne works were 38 per cent. and in 1870 25 per cent., but nowadays certain American works have reduced the loss to 13 per cent. and even 10 per cent. Moreover, the consumption of coal was formerly 10 tons per ton of zinc, but is now, with better furnaces, 3 tons for the producers and 1·2 ton to reduce 3 tons of ore; 500 kilos of refractory material are also used per ton of zinc. Labour has been reduced to one-third and the retorts now last 30 to 40 days instead of 15 to 20 days. Practical tests carried out in Scandinavia over a period of several months show that electric furnaces are not economical for heating the ore; at least 1100 to 1400 kilowatt-hours are required to melt 1 ton of ore, and the wear of the electrodes is more costly than that of the retorts. With large electric furnaces taking 4 tons or more of ore it may, however, be convenient to use electricity instead of coal (Sweden has energy at a cost of 0·05*d.* per kilowatt-hour). In the United States the heating is effected with natural gas (*see* Vol. II., "Organic Chemistry": Methane) in the case of about one-half of the output.

Various attempts have been made to obtain zinc from blende in the electric furnace by heating the ore in presence of iron: $ZnS + Fe = FeS + Zn$. To lower the temperature of the reaction Fitzgerald (1911) mixed 1 part of oxide of iron with 3 parts of ferrous sulphide, and thus obtained at about 1000° a fused mass capable of dissolving 6 parts of blende.

---

[1] According to F. Eulenstein (1912) the thermal balance per 100 kilos of zinc prepared is as follows:

Calories Supplied

By producer gas	1,594,970,	*i. e.*	90·94 %
,, charge	3,230	,,	0·18
,, coal burnt	155,230	,,	8·74
,, the retorts introduced	2,410	,,	0·14
	1,755,840	,,	100·00

Calories Dispersed

Flue gases	891,900,	*i. e.*	50·85 %
Ash	46,790	,,	2·67
Crude zinc	7,960	,,	0·65
Endothermic reactions	191,150	,,	10·76
Retorts removed	3,350	,,	0·19
Gas from the collectors	48,390	,,	2·76
Radiation and loss	565,300	,,	32·12
	1,755,840	,,	100·00

After recovery of the zinc there remains a slag from which the iron may be separated. The whole operation is carried out in a suitable electric furnace.

The crude zinc thus obtained contains various impurities : 1 to 5 per cent. Pb and a little Fe, Cd, Sb, As, Ag, Cu, and also sulphur derived from the blende. The metal is refined by melting it in iron pans, and allowing it to cool slowly in such a manner that almost all the impurities collect at the bottom and at the surface, and may then be easily separated. To-day, however, refining is more often conducted by melting in a reverberatory furnace with an inclined hearth at a moderate temperature for several days. Zinc oxide and other impurities separate at the surface, whilst Pb and Fe collect below.

The pure molten zinc (with 1 per cent. Pb and a little Fe and As) is poured into moulds in order to be worked later. If an exceptionally pure product is desired, the zinc is dissolved in sulphuric acid, and the solution of the sulphate decomposed electrolytically. The zinc which separates is then distilled *in vacuo*. To obtain zinc free from lead, ore free from lead must be used.

ELECTROLYTIC PROCESSES. Various processes have been tried for obtaining zinc from the ores by passing through the sulphate or chloride. Calamine and blende rich in iron do not lend themselves to such treatment. Owing to the strong positive character of the zinc there is a considerable loss of energy (voltage = 4) and in the electrolysis both of solutions of zinc sulphate (from blende slightly roasted) with lead peroxide anodes and of zinc chloride solutions with carbon anodes, the zinc separating is always spongy (with highly concentrated, feebly acid solutions and a high-current density the zinc is less spongy and more compact), and loss is involved in rendering it compact by fusion. With anodes of crude zinc and a voltage of only 1, very pure zinc is obtained at the cathode, but it is always more costly than ordinary refined zinc obtained from minerals free from lead. Electrolysis of alkaline solutions yields zinc dust directly. The problem of electrolytic zinc is hence not yet definitely solved, although certain American works have recently succeeded, under specially favourable conditions, in obtaining compact electrolytic zinc capable of competing with that given by the ordinary processes.[1]

PROPERTIES. Metallic zinc has a greyish-white appearance, and when pure and fused has a specific gravity of 6·91. At ordinary temperatures it is somewhat brittle, but at 100° to 150° becomes ductile and can be rolled into

---

[1] In recent years large electrolytic plants for making zinc have been erected in Japan (at Kosaka and elsewhere), Australia (at Risdon, Tasmania, production started in 1907), Canada (at Trail, British Columbia, and later at Nelson with the French process), where in 1916 2600 tons of electrolytic zinc were produced, and in the United States (Great Falls, Montana; Park City, Utah; Kennett, California and Kellogg, Idaho), where 12,600 tons were turned out in 1916. Electrolytic plants cost more than double as much as furnace plants.

In the Trail works use is made of a mixed ore (iron pyrites, blende, and galena, this coming from the Sullivan mine (East Kootenay) 250 miles away, and containing 21·7 per cent. Zn, 13·8 Pb, 24 Fe, 23·7 S, 5·4 SiO_2, 4·1 Al_2O_3, 1 CaO, a little silver (100 grams per ton) and traces of gold. The ore is first coarsely broken, then finely powdered in tubular ball mills and carefully roasted in eight-floor mechanical furnaces of the Wedge type (p. 295) with coal, the temperature not being allowed to exceed 650°, since otherwise the ore agglomerates; such a furnace turns out 40 tons of roasted ore per day. The sulphur dioxide evolved is used for making sulphur dioxide and the roasted ore still contains 3 to 5 per cent. S, one-half as insoluble sulphide. The ore is next cooled with a water-jet and lixiviated systematically in large vats with 6 per cent. sulphuric acid, the sand and many coarse impurities being separated, and the turbid solution transferred to large metal tanks with conical base, in which it is continuously mixed by means of a strong air-jet (also to render the ferrous salts insoluble) until neutralised (with addition of roasted ore if necessary). The dense mass (4 parts solid to 1 part liquid) is discharged into other condensing vats provided with special stirrers which collect and separate the suspended solid, the mass passing to the second being more fluid (1 part liquid and 1 part solid); the thick paste separated is treated apart with dilute sulphuric acid to dissolve the remaining zinc, and the acid solution thus obtained used to treat fresh roasted ore. The fluid mass containing the zinc dissolved as sulphate passes to the settling vessels, and the clear, yellowish, decanted liquid filtered under pressure; to remove the little copper and cadmium it contains, the solution is passed over granulated zinc, which precipitates these metals, and after further filtration the liquid, containing 6 to 8 per cent. Zn and 0·002 per cent. Fe, is ready for electrolysis. The anodes used are leaden sheets 3 mm. thick, and the cathodes aluminium sheets 2·5 mm. thick; on the latter compact zinc is deposited, this being removed with a knife (after washing with water; the solution, which is originally at 25° and neutral, has 5 to 6 per cent. of acidity at the end and is used to treat fresh ore). Each cathode of 65 cm. side yields at a time 9 to 10 kilos of zinc, this being fused in graphite crucibles out of contact with the air. Current at 3 to 3·5 volts is used, about 4·5 kilowatt-hours being consumed per kilo of zinc. Each battery has 32 cells and yields about 2500 kilos of zinc per twenty-four hours. The leaden anodes last well, as they become covered with a thin layer of manganese dioxide.

sheets. At 200° it again becomes brittle, and can then be powdered. It melts at 419° and boils at 930°. At higher temperatures it catches fire with a greenish-yellow flame and produces a light white powder of zinc oxide (philosopher's wool); it does not alter in dry air and in non-aerated water. In moist air it becomes covered with a thin layer of oxide and carbonate, which preserves it from further alteration, but when present on galvanised (zinc-coated) iron or zinc-coated wires no oxidation of the iron takes place, because the zinc has a higher electric potential and prevents rusting of a metal of lower potential (p. 523). When cast its sp. gr. is 7·1 and when rolled 7·2 to 7·3.

Zinc dissolves easily in dilute H_2SO_4 and in HCl with evolution of hydrogen, but when very pure it is not attacked by these acids, because its surface becomes covered with a very thin layer of hydrogen, which protects it. It decomposes water only at a red heat, but when in the form of an extremely fine powder this decomposition of water occurs in the cold. With hot alkaline solutions it evolves hydrogen :

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Much zinc is used for zinc-coated wires for telegraphy, for roofing, and for the manufacture of zinc-coated (" galvanised ") iron. It is also used for gutters, conduits, baths, etc., because it withstands the action of water very well. It is used in the preparation of various alloys, such as brass, German silver, etc. G. Tammann and N. Raydt (1913) succeeded in obtaining zinc-iron alloys with 11 to 26 per cent. Fe by heating the mixed metals under pressure (at ordinary pressure the zinc distils); the mixed crystals contain $FeZn_3$ and $FeZn_7$. *Zinc dust* is also used for coating iron and steel with zinc in the preparation of lithographic plates, in which case it is spread in a thin layer over the surface, mixed with reducing agents, and then heated in suitable furnaces. Large amounts of zinc dust are used as a reducing agent (for generating nascent hydrogen) in making many organic products (*e. g.*, benzidine, tolidine, etc.; *see* Vol. II., " Organic Chemistry ") and in the printing and dyeing of textile fibres (hydrosulphite vat dyeing, etc.). Certain poor qualities of zinc dust contain as much as 40 to 50 per cent. of ZnO and 3 to 5 per cent. of $ZnCO_3$, besides 2 to 3 per cent. Cd (the cadmium is then extracted) and 2 to 3 per cent. Pb. Good zinc dust contains 79 to 95 per cent. Zn.

The world's production of zinc was 250,000 tons in 1880 and 571,000 in 1903, and in subsequent years it increased rapidly in all countries.[1]

[1] The production and consumption of zinc in different countries are as follows (tons):

Country		1905	1909	1910	1911	1912	1913	1914	1915	1916
Germany	prod.	197 000	220,000	227,000	250,400	271,060	282,000	—	—	—
	con.	—	188,000	178,000	221,800	226,000	—	—	—	—
Belgium	prod.	146 000	164,500	172,000	195,090	200,000	196,000	—	—	—
	con.	—	64,500	78,500	64,900	67,700	—	—	—	—
United States	prod.	183,000	236,600	251,000	267,700	310,000	316,000	500,000	471,000	620,000
	con.	—	247,000	245,000	253,000	312,000	—	—	—	—
France	prod.	35,000	45,000	50,000	54,000	61,000	64,000	—	—	—
	con.	—	67,000	56,000	82,000	82,000	—	—	—	—
England	prod.	51,000	58,400	63,000	66,950	57,200	59,000	—	—	—
	con.	—	155,000	178,000	176,000	185,000	—	—	—	—
Russia	prod.	7,600	8,000	8,600	9,950	14,800	16,000	—	—	—
	con.	—	18,400	25,000	29,500	29,000	—	—	—	—
Austria	prod.	9,000	12,000	13,000	16,000	19,000	21,000	—	—	—
	con.	—	32,800	33,800	43,500	46,900	—	—	—	—
Australia	prod.	6,600	1,070	500	1,727	2,296	3,500	—	—	—
	con.	—	—	12,400	16,200	—	—	—	—	—
Norway	prod.	—	—	—	6,680	8,128	—	—	—	—
	con.	—	—	—	—	—	—	—	—	—
Holland	prod.	14,000	19,000	21,000	22,730	23,930	24,500	—	—	—
	con.	—	4,000	4,000	4,000	4,000	—	—	—	—
Spain	prod.	—	6,100	6,537	8,000	9,500	9,000	—	—	—
	con.	—	4,500	4,300	4,500	4,700	—	—	—	—
World Production		658,700	772,000	816,600	895,000	977,000	995,000	—	—	—
Value . .		—	£17,480,000	£18,800,000	—	—	—	—	—	—

The price was £20 per ton in 1860 and £18 8*s.* in 1902, when the first melt cost £20 to £24; zinc dust cost about £20 per ton and sheet zinc £24 to £28. An international syndicate, established in 1909, regulated the price of zinc up to 1914. In July 1917, during the European War, zinc of the first melt cost up to £120 per ton and zinc dust up to £180 per ton; in July 1918 block zinc sold in Italy at £160 and sheet zinc at £308.

ZINC OXIDE : ZnO. This is obtained by roasting the various zinc ores or by burning zinc in the air (philosopher's wool), or by transforming blende into $ZnSO_4$ and then precipitating with NH_3, or by heating it to redness with carbon: $ZnSO_4 + C = ZnO + CO + SO_2$.

Industrially a good zinc oxide or zinc white is obtained by heating zinc scrap in suitable flat retorts 1 metre long, 0·35 metre wide, and about 0·10 metre high, arranged in furnaces and heated to about 300°, the air supply passing over the surface of the zinc being regulated so that the zinc burns steadily; the zinc oxide passes in very fine powder into channels leading to a flue which carries it to a number of communicating small settling chambers. The zinc oxide in the chambers near the retorts contains zinc dust, but that in succeeding chambers gradually increases in purity. It is purified by blowing it into large chambers divided into compartments by cloth partitions, so that the air is forced to pursue a zig-zag path, and thus deposits the zinc oxide dust carried with it.

With the Wetherill system used in America to obtain zinc white directly by roasting the ore, more than 1000 kilos of coal are consumed per ton of ore treated.

Since 1906 the Monteponi Company (Sardinia) has aimed at obtaining zinc oxide directly from relatively poor calcareous dolomitic gangue, and after various trials in a small factory at Bellavista, a large works was erected at Scalo (near Monteponi) and began to work in 1914; the production of 1600 tons in 1917 is capable of being doubled. The broken ore is pulverised in ball mills, then lightly roasted, and afterwards mixed with lean coal dust (Sardinian anthracite) and converted into briquettes, which are charged into convertors (*see* chapter on Iron) lined with firebrick. The mass is ignited and air blown in to expel the moisture, the gases being directed into a bell and into flues to recover material carried over. When a temperature is reached such that vapour of reduced zinc begins to form, the converter is placed below the combustion chamber, in which the zinc vapour and the carbon monoxide from the converter are completely burnt (the heat of the vapour and of the hot gases may be used for heating steam boilers). The vapours, cooled somewhat, then pass into large chambers with sacking across them, this filtering the gas and retaining the zinc oxide, which is then collected. The product is somewhat less white than that prepared from zinc, and contains about 8 per cent. of lead as sulphate, which gives it increased covering power and the property of mixing well with oil without further grinding.

The production of zinc in Italy was always small: 300 tons in 1909 and 258 in 1916. Spain produced (tons):

	1915	1916
Zinc ore	81,922	166,053 (£259,315)
Sheet zinc	1,715	1,775 (£50,017)
Block zinc	1,489	1,895 (£106,120)
Refined zinc	4,913	4,913 (£127,980)

England has always imported much zinc (about 120,000 tons per annum), the amount being 132,000 tons in 1913, 105,000 in 1914, and 68,000 in 1915.

The United States in 1910 produced 235,000 tons of zinc from native ore and 15,000 tons from imported ore (13,000 in 1911); Illinois produces 70,000 tons, Kansas 105,000, and Oklahoma 34,000. In 1910 there were 224 furnaces with 95,200 retorts (107,000 in 1913). The imported ore had a mean content of 40 per cent. Zn. In 1912 19,000 tons of ore (£140,000) were exported and 10,000 tons of crude zinc (£240,000) imported (in 1911 only 600 tons), besides 2200 tons of zinc dust (£52,000).

During the European War the output of zinc in the United States increased rapidly—from 300,000 tons in 1913 to about 600,000 in 1916—and there was also a corresponding increase in the importation of zinc ore—from 25,000 tons in 1913 to 127,000 in 1915 and 345,000 in 1916 (129,000 from Mexico, 29,000 from Canada, and 122,000 from Australia). In 1915 770,000 tons of blende and 307,000 of calamine were worked, and in 1916 1,090,000 tons of blende and 462,000 of calamine. The mean strength of the ore treated was 45 to 50 per cent. Zn, about 14 per cent. of the total zinc being lost. The number of retorts was 140,000 in 1915 and exceeded 220,000 in 1916, with a mean annual output of 3·3 tons of zinc per retort (in normal times each retort gives 3·8 tons of zinc). The zinc exported was negligible before the European War, but reached 180,000 tons in 1916.

Zinc oxide may also be obtained by calcining basic zinc carbonate, which forms a white powder erroneously called zinc white and is employed in varnishes because it has good covering power and is not blackened by H_2S in the same manner as white lead (basic lead carbonate), but three coatings of white lead on wood produce the same effect as four coatings of zinc oxide, because the latter has less covering power.

When heated it assumes a yellow colour, but becomes white again on cooling. It gives a green colour when heated with cobalt salts.

Calcination of a mixture of about 88 per cent. of zinc oxide and 12 per cent. of cobalt oxide yields zinc green or cobalt green or Rimmann's green, which is used as a pigment, and was produced in Italy to the amount of about 25 tons (£1200) in 1915.

Zinc oxide costs £20 to £28 per ton (in 1895, £14 16*s.*).[1]

ZINC PEROXIDE : ZnO_2. This compound is obtained from $BaO_2 + ZnSO_4$, and is used medicinally for healing wounds.

ZINC HYDROXIDE : $Zn(OH)_2$. This compound is separated from soluble zinc salts by sodium hydroxide or ammonia, but dissolves in an excess of the precipitating agent, because it forms $Zn(ONa)_2$, which is not stable, and dissolves in ammonium hydroxide for the reasons explained in dealing with $Mg(OH)_2$ (p. 671).

ZINC CHLORIDE : $ZnCl_2$. This compound is formed on dissolving zinc in HCl and evaporating the solution, or by heating zinc in a current of chlorine.

It is obtained on a large scale in concentrated solution by treating a solution of a zinc salt with ferrous chloride and passing a current of air through the liquid; all the iron is precipitated and pure $ZnCl_2$ remains. The anhydrous compound (*butter of zinc*) is obtained by heating $ZnSO_4$ with NaCl or $CaCl_2$, when pure $ZnCl_2$ distils. This compound is very hygroscopic and very soluble in water: 100 parts of cold water dissolve 300 parts of the chloride and 100 parts of alcohol dissolve 100 parts, the solution depositing crystals, $ZnCl_2,C_2H_5{\cdot}OH$. Hot solutions lose a little HCl (in the same way as those of $MgCl_2$) and a little basic chloride or oxychloride is formed, but if the solution is kept acid during the heating by addition of a little hydrochloric acid, this decomposition is avoided, and at 0° the solution then deposits crystals of trihydrated zinc chloride, $ZnCl_2,3H_2O$, melting at 7°. It is poisonous, and abstracts water from organic substances to such an extent that they are carbonised. With ZnO the concentrated solution forms a mass which hardens rapidly, this being **Zinc Oxychloride, $ZnOH{\cdot}Cl$.**

It is employed for impregnating woodwork, which is then more resistant against natural decay (*see* Vol. II., chapter on Tar). It is also used as a disinfectant for preserving certain animal preparations and for preparing parchment paper, etc.; mixed with ammonium chloride it is used for soldering.

Solutions of 50° Bé. cost from £6 to £10 per ton, whilst the pure, white, fused product costs double that amount. Italy produced 150 tons in 1905, 400 tons in 1906, and 500 tons in 1908, of the value of £6000, 80 tons in 1914, and 50 tons in 1915.

ZINC SULPHATE : $ZnSO_4$. This is obtained on dissolving zinc in sulphuric acid,

---

[1] The extent of the Italian trade in zinc oxide is shown in the following table (tons):

	1908	1910	1912	1913	1914	1915	1916	1917
Production .	860	1096	1472	1722	2001	2564	1537	—
Importation .	2025	2001	2550	2983	2348	1832	1376	805
Exportation .	395	956	2164	1313	1219	2560	1294	482

England imported 13,500 tons of zinc oxide in 1909, 15,000 tons (£320,000) in 1910, and 17,500 tons in 1911, when 2000 tons (£46,000) were exported.

The United States produced 68,000 tons (£1,280,000) in 1909 and 78,000 in 1910.

France consumed 6000 tons of the oxide in 1900 and exported 3812 tons in 1913, 3213 in 1914, and 3309 in 1915. About 14,000 tons of lithopone were consumed in France in 1913, about 8000 tons being imported; 5000 tons were produced by the Comines Works and 1000 tons at the Ham (Somme) works.

or by roasting the sulphide and then treating it with hot dilute H_2SO_4; any copper which may be present as an impurity is removed from this solution by the introduction of a sheet of zinc, and any iron by boiling it for a long time. It forms crystals of $ZnSO_4, 7H_2O$, very soluble in water (1 : 1·38 at 10° or 1 : 1·65 at 100°), and is isomorphous with various other sulphates (*see above*). It loses $6H_2O$ at 100°, and the seventh molecule of water on heating to redness.

It is used for the preservation of wood and hides, and for rendering fabrics fireproof. It is also used as a disinfectant, as a mordant in textile printing, and in medicine.

The crude crystalline salt costs £4 to £4 16*s*. per ton, and when refined £10 to £12 per ton.

In 1905 Germany produced 5896 tons and Italy 5 tons, apart from that which was imported.

ZINC HYDROSULPHITE : $2ZnS_2O_4,Na_2SO_3$. This is used in indigo dyeing and is obtained by the action of zinc dust on a sulphite.

ZINC CARBONATE : $ZnCO_3$. This is found as *spathic zinc ore, calamine* or *smithsonite* in rhombohedral crystals isomorphous with calcite. It is also formed, mixed with the hydroxide, by precipitating a soluble zinc salt with Na_2CO_3, or with $KHCO_3$ in order to obtain it pure, and is sometimes used instead of zinc white.

ZINC SULPHIDE : ZnS. This compound is found in nature as zinc blende, coloured brown by iron oxide and other impurities, whilst when obtained by precipitation of a zinc salt with ammonium sulphide, it forms a white mass, being the only metallic sulphide of this colour.[1] Zinc blende is fluorescent after having been submitted to the action of sunlight and even at the temperature of liquid air if it has been exposed to the action of radio-active emanations (Occhialini and Chella, 1907).

Blende occurs in abundance in Bohemia (Ratieborsitz, Schlackenwald), Hungary (Kremnitz, Chemnitz), Germany (Freiberg, Andreasberg,) England (Cornwall), Transylvania (Rodna and Kapnik), the United States, Sweden, Norway, and Sardinia.

For obtaining zinc and SO_2 or sulphuric acid, 453,750 tons of blende were worked in Germany in 1908, 650,000 in 1910, and 554,760 in 1912.

Various patents have been taken out in recent years for the industrial preparation of this sulphide (Ger. Pats. 149,557 and 167,498, etc.).

Molten sulphur reacts with difficulty with zinc, whilst a mixture of zinc dust and powdered sulphur reacts violently on heating.

It is insoluble in water but soluble in dilute acids, excepting acetic acid, and therefore when it is to be precipitated from its salts with H_2S, sodium acetate must be added to saturate the acid liberated from the zinc salt. It is fluorescent, as are the alkaline earth sulphides. When white it costs £48 per ton.

LITHOPONE. By precipitating a hot solution of zinc sulphate with a hot solution of barium sulphide, a white precipitate is produced which is filtered, 1 per cent. of freshly precipitated magnesium hydroxide added, then dried, pulverised, mixed with 3 per cent. of ammonium chloride, heated to redness, and poured into water whilst still hot. It is then again dried and finely ground; *lithopone* is thus obtained, which is a mixture of zinc sulphide and barium sulphate, containing 11 to 42 per cent. of ZnS; the so-called yellow quality contains 11 to 18 per cent. of ZnS, and costs about £14 8*s*. per ton, whilst the blue quality, containing 22 to 30 per cent., costs £18 8*s*., and the green quality, containing 32 to 42 per cent., costs up to £21 12*s*. per ton. It can advantageously be used instead of white lead because it has somewhat better covering power, and is not poisonous (*see* the various patents, Ger. Pats. 163,435, 166,717, 166,772, and 170,478); it is also called zinc white. In analysing lithopone it is desirable to determine not only the zinc, but also the sulphur.

Germany exported 5820 tons of lithopone in 1890, 8623 tons in 1900, and 9500 tons of the value of £136,000 in 1907, in which year 2200 tons were imported.

Lithopone to the value of £220,000 was produced in the United States in 1909.

Most of the lithopone used in Italy is imported from Germany; the imports amounted to 196 tons in 1908, 381 in 1910, and 486 in 1913.

---

[1] *Translator's note.*—This remark refers to those metallic sulphides only which are encountered in the ordinary course of analysis.

ZINC PHOSPHIDE, Zn_3P_2. This is obtained in various ways, *e.g.*, by heating zinc dust in phosphorus vapour, or by heating a mixture of zinc dust and red phosphorus in a current of hydrogen and lighting gas. The phosphide has a grey metallic appearance, a vitreous fracture, and the smell of phosphorus; it resists the action of water, but acids decompose it with liberation of hydrogen phosphide. Another phosphide, ZnP_2, is also known, and forms reddish-yellow crystals, becoming red when heated. The first phosphide is used to a small extent in pharmacy, but it is now largely employed to combat rats and mice, for which purpose it is mixed with maize. Barium carbonate and lead arsenate are less efficacious, while some maintain that more certain results are obtained with contagious, pathogenic viruses formed, *e. g.*, by Loeffler's or Danysz's bacterium.

CADMIUM: Cd, 112.4

This element often accompanies zinc in its ores (about 0·4 per cent., though calamine, for example, sometimes contains up to 5 per cent. in Silesia and Missouri). It is easily separated, because it distils before the zinc, or by means of its sulphide, which is insoluble in dilute mineral acids, whilst zinc sulphide is soluble. On roasting zinc blende a considerable portion of the cadmium remains in the residue in the form of sulphate and may be extracted with water (U.S. Pat. 799,743); about 80 per cent. of the cadmium in zinc ores is lost in the treatment of these ores. Pure cadmium is obtained by treating a mixture of Zn and Cd with dilute H_2SO_4, as by this treatment all the zinc is first dissolved. Cadmium is a somewhat soft white metal, of sp. gr. 8·6, which melts at 321° and boils at 770°. It does not alter in the air, but becomes covered with brown oxide on heating. It dissolves more easily in dilute HNO_3 than in dilute HCl or dilute H_2SO_4. It has been found that cadmium vapours at 1700° consist of monatomic molecules. It is used as an addition to various metallic alloys in order considerably to reduce their melting-points. With mercury it forms a soft amalgam which then hardens very easily, and for this reason is used as a cement for stopping decayed teeth. The world's production of cadmium was 3 tons in 1880 and 13 tons in 1902, whilst in 1905 Germany alone produced 24·5 tons; in 1910 the world's consumption was about 40 tons, part of this being produced in the United States. The price to-day oscillates round 8*s*. per kilo.

CADMIUM OXIDE : CdO. This compound is formed on burning cadmium in the air or on heating the sulphate, carbonate, or nitrate. It is obtained as a brown powder of sp. gr. 6·95, or in bluish-black microscopic crystals of sp. gr. 8·1.

CADMIUM HYDROXIDE : $Cd(OH)_2$, is obtained from cadmium salts with sodium hydroxide, and dissolves in ammonia.

CADMIUM CHLORIDE : $CdCl_2 + 2H_2O$, is more stable than $ZnCl_2$ and does not, therefore, yield HCl on heating with water. It melts at 540° and sublimes.

CADMIUM BROMIDE and IODIDE are used in photography.

CADMIUM SULPHATE : $CdSO_4$. This compound is obtained from Cd and H_2SO_4 and crystallises with $7H_2O$ in a form isomorphous with the sulphates of Zn, Mg, etc. A hydrated sulphate, $5CdSO_4,8H_2O$, is also known.

CADMIUM SULPHIDE : CdS. This is obtained from soluble cadmium salts by precipitating them with H_2S or sodium sulphide, and forms a mass of bright orange-yellow colour, which is used in painting, as it is resistant to the action of light and also has very good covering power. It costs from 8*s*. to 12*s*. per kilo.

MERCURY: Hg, 200

This metal was known under the name of quicksilver 300 years before Christ, and was studied by the alchemists (*see* p. 14).

Mercury is the only metal liquid at the ordinary temperature, and is only rarely found free or as silver amalgam in nature. It is found, on the other hand, almost exclusively as cinnabar, HgS, in Spain (at Almaden, where it has been mined from the time of the Romans), Mexico, Austria (Idria from A.D. 1500), Peru, China, Japan, California (at New Almaden, from 1850), Russia (at Nitikowka, in the south), and Tuscany (at Monte Amiata).

Almost the whole of the mercury is obtained on distilling cinnabar in suitable furnaces in presence of an abundant supply of air. The mercury thus distils together with sulphur dioxide, and on cooling the receivers it condenses, whilst the SO_2 is then dissolved in water. The mercury is obtained practically pure by redistilling it from iron vessels.

The type of furnace which was used some years ago at Idria for the treatment of cinnabar is illustrated in Fig. 265. In the central portion there is a furnace with three perforated hearths, *a*, *b*, and *c*, on to which the ore is charged according to its size, and it is then roasted by the hot gases formed in the hearth below. The mercury vapours, mixed with SO_2, condense in a series of lateral chambers, *C*, and the liquid mercury runs on to an inclined floor and collects in a single channel outside.

The uncondensed gases (SO_2) are absorbed in the last chamber, *D*, down which a current of water passes along inclined planes, and the aqueous solution of SO_2 which is so obtained is utilised. This process is, however, not continuous, and does not give a good yield. In 1890, therefore, the above furnaces were replaced by reverberatory and cupola furnaces, which permit of continuous working with yields of about 90 per cent. Similar furnaces, improved by Scott, are used in California.

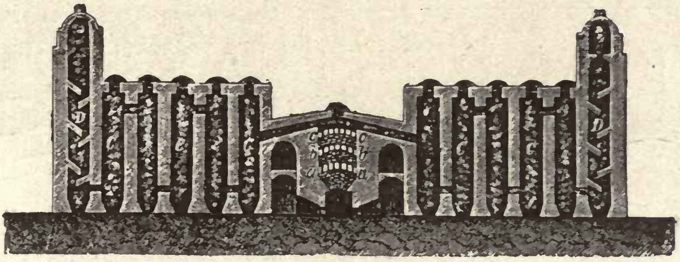


FIG. 265.

Since 1890 Cermak-Spirek furnaces have been largely used in all localities where mercury is smelted. The engineer Spirek gave an interesting account of these furnaces at the International Chemical Congress at Rome in 1906. The ore falls automatically from above down channels formed of inclined planes along which the ore passes, being thus stirred up, and then over other lower inclined planes, which become hotter towards the bottom. The gases rise in a direction contrary to the descending stream of ore and carry off the mercury vapours together with the other gases (H_2O, CO, CO_2, air, H_2SO_4, SO_2, etc.) and with ash.

The whole of the hot gases pass to the condensers where the vapours of H_2O, SO_2, and NH_4Cl are first cooled in inverted stoneware U-tubes down the outside of which water passes, each of which dips into a wooden vat. The mercury is here separated, together with solid impurities, and collects partly in the vats and partly on the walls of the tubes, forming "soots" which contain some mercury, and are treated separately. The remaining gases, which still contain mercury, pass through conduits, where they are filtered by traversing a long path through wooden laths arranged like Venetian blinds. In this way further "soots" are formed and all the mercury is deposited. The whole apparatus is maintained at a slightly diminished pressure by means of a fan in order to avoid leakage towards the outside. With the Cermak-Spirek plant poor ores containing less than 1 per cent. of Hg may be treated, and the mean loss does not exceed 5 per cent. of the mercury.[1]

---

[1] This plant was tried in 1907 in a works at Rescaldino, for desulphurising and oxidising cupriferous burnt pyrites which was to undergo electrolytic extraction of the copper, but apparently without practical success.

In Fig. 266 the complete plant used at Monte Amiatá is shown, including the furnace, *A*, condensers, *B*, and the filters, *C*. Fig. 267 shows a transverse section of the furnace with inclined walls, forming channels down which the ore moves, thus descending from the top to the bottom.

Some years ago (1905) a new furnace was introduced in some districts, called the Dennis furnace. This consists of a number of small superposed chambers down which the ore passes from the top to the bottom of the furnace, being met by an opposed current of hot gases from a wood-gas producer. The temperature rises gradually from 200° to 300° in the upper drying chambers, and in the lower ones the roasting temperature reached before the ore leaves the furnace is 800° to 850°. The ore passes completely through the furnace in about four hours (with the old ones twenty-four hours were required); the yields appear to be good. This furnace was used at Oregon, but production ceased there in 1911.

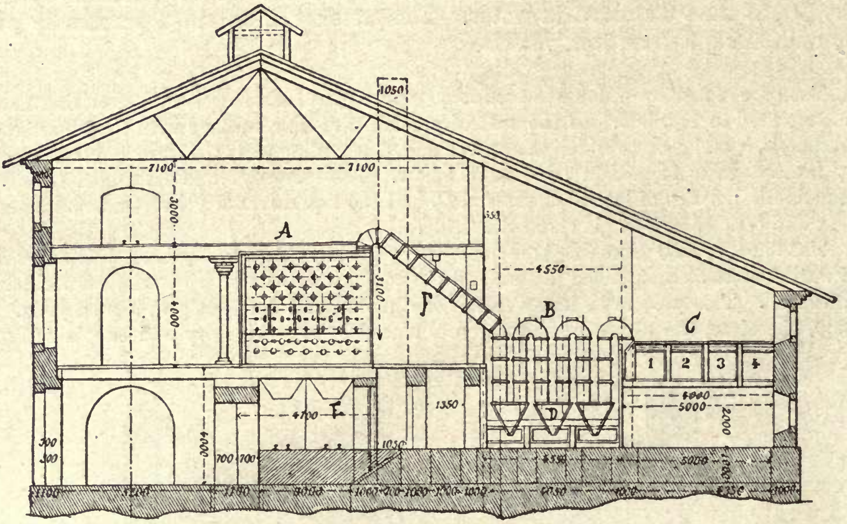


FIG. 266.

Whatever the type of furnace employed, only 20 to 50 per cent. of the mercury is obtained in the liquid state, the rest forming a more or less pulverulent mass (called *stupp*) containing droplets of mercury, mixed with Hg_2O, $HgSO_4$, HgS, soot, tar, and water. This is mixed with a little quicklime to fix the water and acid products, and then passes to a special Exeli press, formed of a stationary cylindrical iron vessel furnished with various series of vertical knives; a vertical axis carries horizontal arms to which knives are fitted, so that when the axis revolves, the mass is crushed between the fixed and moving knives, the drops of mercury being pressed out and discharged through channels at the base of the vessel. By this treatment the mass loses quite one-half of its mercury, but still contains 10 to 20 per cent.; it is formed into cakes and returned to the furnace with fresh ore.

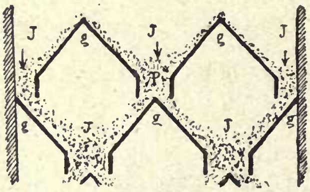


FIG. 267.

In some places mercury is obtained by heating a mixture of cinnabar and iron or lime, which retain the sulphur, whilst the mercury distils:

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Attempts have lately been made to extract the mercury from cinnabar electrolytically by suspending it in a solution of NaCl or KCl; an E.M.F. of 1 volt suffices to cause a separation of mercury at the cathode. This method presents the great advantage of eliminating all danger of poisoning by mercury vapours, which is such a cause of anxiety when working by dry methods.

Mercury is purified by redistilling it and then squeezing it through sacks or closely woven cotton fabrics. In order to separate dissolved traces of other metals, the mercury is then poured in a thin stream down tall cylinders containing cold, dilute nitric acid (8 to 10 per cent.), which dissolves the other metals more easily than the mercury; it is then washed with water and dried.

PROPERTIES. Mercury is a liquid of silvery appearance. It does not alter in the air, has a specific gravity of 13·596 at 0°, solidifies in octahedra at — 38·87°, and boils at 357·3°. When near its boiling-point it becomes covered with a red layer of HgO, which decomposes at 500° into $Hg + O$. The critical temperature of mercury vapour appears to be about 1650°.

In those compounds in which mercury behaves as a divalent element of the type HgX_2 the resemblance with zinc and cadmium derivatives is very marked, so much so that the various double salts are sometimes isomorphous, for example, $HgSO_4,K_2SO_4 + 6H_2O$. But mercury is distinguished from these metals by forming a series of compounds HgX, where the mercury acts as a monovalent element. We shall see below that various other elements exercise variable valency, as was already noted in dealing with the non-metals. When a metal forms two or more series of combinations, the chemical and physical differences between the compounds of such classes are greater than those between two metals of the same group.

Mercury vapours were the first in which monatomic molecules were discovered. In the cold it is only slightly attacked, or not at all, by HCl or H_2SO_4, whilst on heating with H_2SO_4, $SO_2 + HgSO_4$ and H_2O are formed. It readily combines with the halogens and with sulphur. It dissolves almost all the metals excepting iron, forming amalgams. Tin amalgam is used for mirrors. On studying amalgams by means of their freezing-points and also microscopically, it is found that chemical compounds between the components of the amalgams are sometimes formed, such as $HgNa_2$; on the other hand, they often form true solutions or mixtures, and in certain cases mixed crystals are formed.

A new mercury electric lamp (Bastian) has recently found application, and gives an intense and economical but greenish light. It consists of a glass tube, 50 to 60 cm. long, containing a little mercury and two electrodes at its ends. A very high vacuum is then produced in the tube, which is placed horizontally, and an electric current is passed along a thread of mercury uniting the two poles. The mercury is thus rapidly heated, and when mercury vapours have been formed these conduct the current, which no longer requires the liquid mercury in order to pass. The vapour becomes incandescent, emitting a very intense light, and the tube should then be inclined in order to collect all the mercury at one end. The disadvantage of these lamps, which act with an E.M.F. of 50 to 60, or even of 100 volts, consists in the fact that the glass tubes sometimes break through the powerful heat, liberating all the mercury vapour, which is poisonous. A further disadvantage for domestic purposes consists in the fact that it has been observed that the light emitted from the most luminous portions exercises a harmful physiological action. They are, therefore, more suitable for lighting public places, as the consumption of electric current is very small. In order to avoid fracture of the tubes through temperature rises, Heraeus constructs these lamps with a quartz tube, but they are then very dear, and Schott prepares a special tube of sufficiently resistant glass, the light, which is almost devoid of red rays and is too green, being corrected by coloured glasses. The light of these lamps is rich in ultra-violet rays, and in order to utilise these, for example, for the sterilisation of water, quartz tubes are required, which do not absorb these rays. A light which is richer in red rays can be obtained from these lamps by the addition of cadmium or bismuth to the mercury.

The largest quantities of mercury are used for the extraction of gold and silver (*see below*), but it is also used in the construction of numerous physical instruments (thermometers, barometers, pumps, etc.). It is used in the preparation of mercury fulminate, corrosive sublimate, etc., and ointments used in the treatment of skin diseases, and especially syphilitic diseases; many of its derivatives are used industrially and medicinally.

Copper amalgams are also used to treat the keels of vessels to prevent attack by algæ and molluscs (*see later:* Mercuric Oxide). Formerly much mercury was used to prepare amalgam for mirrors.

Mercury forms two series of compounds: *mercurous* compounds, in which one atom of mercury is saturated by one monovalent atom, and which are obtained by various reactions in presence of excess of mercury, and *mercuric* compounds, in which the mercury is divalent and which are more stable.

Mercury is placed on the market in iron bottles which contain a definite weight. Spanish, American, and Italian mercury is sold in bottles containing 34·5 kilos of Hg, whilst those from Russia contain 34·7 kilos, and those from Idria 34·05 kilos.[1]

MERCUROUS COMPOUNDS

MERCUROUS OXIDE: Hg_2O. This is obtained by precipitating a mercurous salt with a solution of sodium hydroxide. It has a dark brown colour and is decomposed into $HgO + Hg$ by light and by carbon.

MERCUROUS CHLORIDE: HgCl (Calomel). This compound is prepared by heating an intimate mixture of 4 parts of powdered mercuric chloride, $HgCl_2$, with 3 parts of mercury in a covered iron pan; the grey mass is heated until it becomes white and on then raising the temperature all the calomel sublimes on to the top of a plate which projects inside the pan. It is then poured into a vat of water and purified by repeated washing with dilute nitric acid to remove remaining traces of unaltered mercury, and is finally washed thoroughly several times with distilled water to eliminate the last traces of corrosive sublimate, which would be poisonous, as calomel is administered medicinally through the mouth. Calomel is obtained also by precipitating a solution of mercurous nitrate with NaCl or by passing SO_2 into a solution of corrosive sublimate, or according to the equation:

$$HgSO_4 + 2NaCl + Hg = NaSO_4 + 2HgCl.$$

It forms a white mass, insoluble in water, alcohol, and dilute acids. It decomposes slightly in the light, forming $Hg + HgCl_2$, and is also decomposed by boiling water. HgCl is blackened by ammonia owing to the formation of **Dimercuro-ammonium chloride, NH_2Hg_2Cl,** mixed with Hg.

At 448° it is converted into vapour, the density of which corresponds with the formula HgCl, but at this temperature it is decomposed into $HgCl_2 + Hg$,

---

[1] For Italy the amounts of mercury made and exported are as follows (tons):

	1905	1910	1912	1913	1914	1915	1916	1917
Production .	370	893	1000	1004	1073	985	1093	—
Exportation .	243	780	993	993	760	853	767	1116

The ore treated was 70,000 tons in 1910, 110,640 in 1915, and 132,524 in 1916. During the European War the output of mercury in Italy increased, and in 1916 was taken over by the Government, who controlled exportation, prices rising to 12*s.* or even 16*s.* per kilo.

France imported 198 tons of mercury in 1913, 167 in 1914, and 330 in 1915, and exported 88 tons in 1913, 54 in 1914, and 12 in 1915.

Spain (at Almaden) in 1904 produced 1020 tons of mercury, in 1906 1568, in 1913 1490, in 1915 1222 (from 20,717 tons of ore), and in 1916 795 tons (£354,647).

England imported 1500 tons (£400,000) in 1910.

At Idria (Austria) 580 tons in 1904, 630 in 1908, and 855 in 1913.

The United States produced 1200 tons of mercury in 1904, 963 in 1906, 680 in 1908, 688 in 1913, and 700 (£200,000) in 1914. The greatest output was in California and the least in Texas and Nevada. To China 250 tons were exported in 1909, but only 70 tons in 1910.

Russia produced 393 tons in 1904, 210 in 1906, and 130 in 1907.

Germany imported 723 tons in 1909.

Mexico produced 190 tons of mercury in 1904, 200 in 1906, and 150 in 1913; the bulk of this is made in the San Luis Potosi district (at Moctezuma and at Guadalcazar 2000 metres above sea-level).

The world's output of mercury was 3308 tons in 1900, 3255 in 1907, and 4170 in 1913.

The price of mercury varies between 3*s.* 2*d.* and 5*s.* 7*d.* per kilo in normal times, and rose rapidly during the European War; thus, in France, 20*s.* 9*d.* to 24*s.* was paid in 1917 and 1918, and in Italy the price was controlled by the Government at 12*s.* 9*d.* in 1916.

which recombine in the cold, and it is therefore probable that the true formula of calomel is Hg_2Cl_2.

It is used in medicine (when absolutely free from $HgCl_2$) and, together with gold, for colouring porcelain. It costs from 5*s.* 7*d.* to 6*s.* 5*d.* per kilo.

Mercurous Bromide and **Iodide** are more stable and less soluble than the chloride and separate mercury in the light. **Mercurous Azide, HgN_3,** is also known.

MERCUROUS NITRATE : $HgNO_3$. This is prepared by the action of one part of mercury on one part of not too concentrated nitric acid in the cold. It crystallises with $2H_2O$. It dissolves unaltered in a little water to form a yellowish basic nitrate, $HgNO_3$, HgO, with much water. It oxidises in the air, forming mercuric nitrate, but this is reduced to mercurous nitrate by excess of Hg. It is a powerful poison.

MERCUROUS SULPHATE : Hg_2SO_4. This compound is formed by the action of concentrated sulphuric acid on an excess of mercury. It is crystalline, only slightly soluble in water, and forms $Hg + O_2 + SO_2$ on heating.

MERCURIC COMPOUNDS

MERCURIC OXIDE : HgO (Red Precipitate). When an equimolecular mixture of mercuric nitrate, $Hg(NO_3)_2$, and Hg is gradually heated in a metallic capsule or in a small muffle furnace, an oxide of a more or less bright brick-red colour is obtained in crystalline scales of sp. gr. 11·2, only slightly soluble in water and very poisonous. The red oxide is also formed when mercury is heated for a long time in the air. If, on the other hand, this oxide is prepared by wet methods, for instance, by pouring a solution of mercuric chloride into a boiling solution of sodium hydroxide, mercuric oxide of an intense yellow colour is obtained which blackens in the light through separation of mercury. The difference between the red and the yellow oxides consists only in the colour, due to the different degrees of fineness of the particles.

Mercuric oxide decomposes alkali chlorides, bromides, and iodides :

$$HgO + 2NaCl + H_2O = HgCl_2 + 2NaOH.$$

When boiled with aqueous NH_3 mercuric oxide forms a yellow solution of **Hydroxydimercuro-ammonium Hydroxide, $OH{\cdot}Hg_2NH_2O$** (*Millon's base*).

It is used medicinally, for colouring porcelain, and for coating or varnishing keels of vessels in order to prevent shell-fish and marine plants from adhering to them. In this way less friction is caused during navigation and considerable quantities of fuel are saved. In contact with the sodium chloride of the sea water, mercuric oxide perhaps forms a little corrosive sublimate which is poisonous to plants and animals. It costs 4*s.* 9½*d.* to 6*s.* per kilo. Italy produced 25 tons in 1907, of the value of £6000.

MERCURIC CHLORIDE : $HgCl_2$ (Corrosive Sublimate). This compound is obtained by subliming a mixture of mercuric sulphate and NaCl in a clay vessel on a sand-bath with the addition of a small quantity of MnO_2; the sublimate collects in white crystals, forming rhombic prisms of sp. gr. 5·4 and melting at 265° : $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. It is also obtained by the wet method, by dissolving HgO in HCl and then evaporating the solution. It is now prepared industrially by passing gaseous chlorine, produced from liquid chlorine, over mercury heated almost to its boiling point, and condensing the sublimate so formed in the crystalline condition in the enlarged, cold portion of the glass retort in which the reaction is carried out. 20 to 25 kilos of mercury are treated in each retort in 8 to 10 hours, and the sublimate is removed by breaking the retort after each operation. According to E. Trutzer (Ger. Pat. 262,184, 1912) it is also obtained by passing chlorine over mercury covered with water at 20° and shaking to break and dissolve the skin of sublimate which forms; that which does not dissolve separates as a white powder.

It is a very powerful poison.

A solution of corrosive sublimate is easily reduced by SO_2 or by stannous chloride with separation of white, insoluble mercurous chloride, which becomes grey with an excess of the reagent through the separation of Hg, thus:

$$2HgCl_2 + SnCl_2 = SnCl_4 + 2HgCl,$$

and then $2HgCl + SnCl_2 = SnCl_4 + 2Hg$.

With ammonia it forms a white precipitate of **Mercury ammonium chloride,** $\mathbf{HgClNH_2}$ **(White Precipitate).** One part of corrosive sublimate dissolves in 15 parts of cold water or 2 parts of boiling water. It is more soluble in alcohol. The aqueous solution shows an acid reaction because it undergoes slight hydrolytic dissociation, and on addition of NaCl the reaction becomes neutral, because the double salt $HgCl_2,NaCl,H_2O$ is formed, which has a less energetic antiseptic action than $HgCl_2$. The action of the other halogen salts is also less energetic, because they are less highly ionised. It melts at 265° and volatilises at about 300° without decomposing. The aqueous solution coagulates protein solutions.

It is used medicinally, as an antiseptic, and also for impregnating the wooden sleepers of railways. It is also used in the manufacture of aniline dyestuffs, in calico printing, and for photographic purposes.

Before the European War corrosive sublimate cost 5*s.* 2½*d.* per kilo. Italy exported 22·8 tons in 1904, of the value of £5472; 39·5 tons in 1905, 30·2 tons in 1907, 9·8 tons in 1908, 21·7 tons in 1909, of the value of £4340, 12·1 tons in 1911, 83·5 tons in 1912, 90·6 tons in 1913, 31·9 tons in 1914, 37·6 tons in 1915, 65·6 tons in 1916, and 15·5 tons in 1917. The production of sublimate and calomel in Italy was 30 tons in 1905, 75 tons in 1908, of the value of £15,000, and 91 tons in 1909. In 1907 Italy produced 100 tons of mercury salts altogether and exported 11·5 tons, exclusive of sublimate. It exported 20 tons in 1908 and 14·8 tons in 1909, of the value of £4120. During the war the price rose to 24*s.* per kilo.

Mercuric Bromide, $\mathbf{HgBr_2}$, is similar to the chloride.

MERCURIC IODIDE: $\mathbf{HgI_2}$. This compound is obtained by precipitating a soluble mercuric salt with a solution of potassium iodide. A yellow crystalline substance is first formed which suddenly becomes red and is very insoluble in water. This iodide suddenly acquires a yellow colour at 130° and melts at 223° to form a red liquid, which on cooling first becomes yellow and then red again. These colours are due to isomeric forms of the same substance. HgI_2 is soluble in a solution of KI, and on adding potassium hydroxide to this solution *Nessler's reagent* is obtained, this being used for the detection of minimal traces of ammonia (for instance, in water: p. 235), with which it forms a brown precipitate. Nessler's reagent is prepared by boiling a mixture of 35 grms. of KI with 13 grms. of $HgCl_2$ in 800 grms. of water, and then adding a cold saturated solution of $HgCl_2$, drop by drop, until a permanent precipitate is just obtained. 160 grms. of solid KOH are then added and the whole is diluted with water to 1000 c.c., after which a further few drops of mercuric chloride solution are added; the whole is allowed to stand and the clear liquid decanted and kept in well-closed bottles. The **Double iodide of mercury and copper,** $\mathbf{HgI_2,CuI}$, behaves in a similar way on heating, but the colour-changes occur at temperatures below 100°, and it has therefore been suggested as a material for colouring the extremities of the axles of railway waggons so that any over-heating through excessive friction may easily be noticed.

The mercuric halogen compounds are very resistant to the action of concentrated H_2SO_4 and also to alkalis.

MERCURIC CYANIDE: $\mathbf{Hg(CN)_2}$. This compound is formed by heating mercuric oxide with Prussian blue (*see* Iron) suspended in water. It then separates on cooling in large colourless prisms. It is more soluble in alcohol and in ether than in water. It resists the action of acids and its aqueous solutions are precipitated neither by $AgNO_3$ nor by KOH, perhaps because they are dissociated into ions only to a minimal amount, and a precipitate of HgS is obtained only with H_2S or with alkali sulphides, because it is very insoluble, and a small number of dissociated ions of the cyanide separate completely as HgS until all the mercuric cyanide has been decomposed.

MERCURIC NITRATE : $Hg(NO_3)_2$. This compound is not easily prepared in a pure state because a little basic nitrate is always obtained with mercury in excess of hot nitric acid. It is very poisonous. On diluting its aqueous solution the insoluble basic nitrate, $Hg(NO_3)_2, 2HgO, H_2O$, separates and produces pure HgO on boiling.

MERCURIC SULPHATE : $HgSO_4$. On heating Hg or HgO with excess of concentrated H_2SO_4 the sulphate separates as a colourless crystalline mass which becomes yellow on heating. It is insoluble in water, in contact with which it forms a yellow basic salt, $HgSO_4, 2HgO$, also insoluble. It forms double salts with the alkali sulphates, for example, $HgSO_4, K_2SO_4, 6H_2O$, which are isomorphous with the corresponding double salts of magnesium, zinc, etc.

MERCURIC SULPHIDE : HgS. This is found in nature as *cinnabar*, a bright red mass of radiating crystals. It is almost always obtained artificially by the dry method by heating the crude black sulphide obtained by mixing and stirring a mixture of 54 parts of Hg and 7·5 parts of sulphur in a covered cast-iron pot. The cinnabar which sublimes forms a bright red crystalline mass which is then ground under water to avoid the production of dust, and is purified by heating it with a solution of potassium carbonate, being afterwards further washed with water, dried on tiles, and finally ground with special precautions. The brightness of its red colour depends on the fineness of its particles.

It is prepared by the wet method by mixing 5 parts of Hg thoroughly with 1 part of sulphur and then heating the mixture to 45° with a concentrated solution of KOH of 45° Bé. until the black powder becomes bright red. It is then poured into water, washed, and dried.

It is obtained in the laboratory by the action of H_2S on a solution of a mercuric salt, and then forms a black mass which becomes red on sublimation. It is used in painting, but the colour fades in time. It is often adulterated with iron oxide, minium, gypsum, etc. It costs 6*s.* to 6*s.* 10*d.* per kilo. Germany exported 199·4 tons in 1905 at £240 per ton. Italy imported 14·7 tons of cinnabar (or vermilion) in 1907, 7·9 tons in 1908, and 7·6 tons in 1909, of the value of £2120.

COPPER, SILVER, AND GOLD

These three elements form a rather heterogeneous group, which is derived from Mendeléev's periodic system of the elements (*see* the end of this work), but forms a weak point in the brilliant conception of the Russian chemist. It is only by forced conceptions that any close analogy can be found between these elements.

Already when we consider their valencies we find that copper is usually divalent in its compounds, whilst silver is exclusively monovalent and gold is sometimes monovalent, but generally trivalent.

Their oxides and sulphides are all insoluble, like those of the heavy metals, and it is only in some reactions that a certain analogy can be traced between the compounds of this group and those of the group of the alkali metals. The heats of formation of those derivatives of these metals in which the latter show minimal valency decrease with increase of the atomic weight.

COPPER: Cu, 63.57

This element is sometimes found in the natural state crystallised in octahedra or cubes, but usually occurs in combination in various minerals (coloured black, blue, or red) in America, Sweden, the Ural Mountains, Japan, and China. It is found as *Chalcopyrite*, CuS,FeS, as basic carbonate in *Malachite*, $CuCO_3 + 3Cu(OH)_2$, and *Azurite*, $2CuCO_3 + Cu(OH)_2$, in *Cuprite*, Cu_2O, and in *Chalcosine*, Cu_2S.[1] It is one of the metals which have been used by man since

---

[1] In Italy copper ores are worked at Agordo (Belluno) (pyrites with about 1·5 per cent. of copper); in Liguria (at Rovegno, Gallinaria, and especially at Libiola), chalcopyrite is worked containing 5 to 13 per cent. of Cu and up to 49 per cent. of sulphur. In the Val d'Aosta (at San

remote antiquity, but its consumption has increased extraordinarily of late years.

The metal may be extracted from poor copper ores by the wet process, whilst in the case of rich ores the dry process is usually applied.

The dry treatment of oxidised ores and of native copper is very simple, as it is merely necessary to heat them with carbon and a siliceous flux in a reverberatory furnace. A very impure copper is, however, thus obtained. The treatment of sulphurised ores is considerably more complicated, but produces a much purer metal.

In order to concentrate poor ores these are pulverised and then introduced into horizontal revolving cylinders with an internal spiral channel (Fig. 268) (English Macquisten process) through which passes a strong current of water which does not moisten the particles of mineral sulphide, so that these float and are continually discharged along the wide horizontal channels, *b*, which enter the cylinders, and through the tubes, *c*. The ore, which contains ten times as much copper as before, finally passes into the common channel, *d*. The particles of siliceous gangue, which contain no metal, are completely moistened by the current of water, collect at the bases of the cylinders on account of their weight, and are carried by the spiral channels into other collecting tubes which lead to the single discharging channel, *e*. The cylinders make 30 revolutions per minute, and may also be arranged in series so that the ore passes from one to the other and there is no danger of loss. Each tube treats from 5 to 6 tons of ore per day. The concentrated ore cannot be introduced directly into the furnace as a powder, because it would cause obstruction; it is therefore moistened, converted into compressed briquettes, and dried, or is slightly melted, so that a species of agglomerate is formed, in Danks' furnaces (*see* Iron).

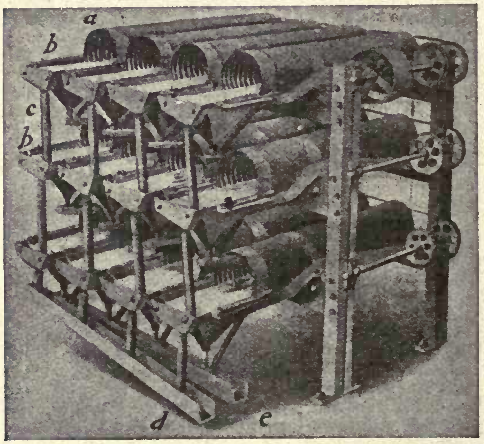


FIG. 268.

(1) **TREATMENT OF SULPHURISED ORES BY THE DRY METHOD.** A considerable portion of the sulphur in these ores is utilised by roasting them in suitable

---

Marcello and at Ollomont) chalcopyrite is also worked. There are various mines in Tuscany and the ore is treated more especially at Leghorn, but if very rich it is sent to England. The mineral which is worked at Massa Marittima also contains tin.

The output, importation, and exportation of copper ores in Italy are as follows (tons):

	1910	1911	1912	1913	1914	1915	1916	1917
Output .	68,369	68,136	86,001	89,487	86,953	74,470	—	—
Imports	8,006	6,885	6,831	1,089	850	571	2,454	467
Exports .	1,025	215	288	285	470	2	—	20

Italy also produced 14,613 tons of cupriferous pyrites in 1915 and 19,836 tons (£23,793) in 1916.

In Spain the output of copper ores was as follows :—

1915, 23,068 tons, of the value £78,579
1916, 25,180 ,, ,, ,, £160,535

England produced 2,569 tons of copper ore in 1913 and 2,373 tons (£12,985) in 1914. The imports were :—

Copper matte or precipitated copper . 65,292 tons in 1909 and 68,974 in 1910
Scrap copper . . . . . . 2,352 ,, ,, ,, 2.948 ,,
Unworked copper . . . . 131,154 ,, ,, ,, 87,447 ,,

the value being £3,000,000 (1910); the exports were valued at almost £760,000.

France exported 10,153 tons of copper ore in 1913, 5,865 in 1914, and 974 in 1915, and imported 9,653 tons in 1913, 10,717 in 1914, and 2,758 in 1915.

furnaces such as are used for the pyrites utilised in the manufacture of sulphuric acid (p. 293). In 1912 the Tennessee Copper Co. produced 200,000 tons of sulphuric acid (60° Bé.) by utilising the SO_2 in leaden chambers with a total volume of 130,000 cu. metres.

Where the sulphur is not utilised the roasting is conducted simply in large heaps containing hundreds of tons of ore in the open air on a layer of wood which is then lighted. The roasting lasts from four to five weeks. In this way a portion of the sulphur and certain volatile products such as antimony and arsenic are eliminated. A more or less finely divided mass of black colour thus remains, the colour being due to the oxides of copper and iron formed. The roasted ore is then treated in some countries in cupola furnaces, whilst in others reverberatory furnaces are used (*see* Fig. 269, section and plan), in which it is mixed with coal (where coal is cheap, as in England, or where the ores contain much antimony and arsenic). Since much time and fuel, and also a portion of the sulphur, are lost during roasting, the crude material is often treated directly in a cupola or reverberatory furnace, the SO_2 being then utilised. This utilisation is, however, not easy on account of the large quantities of other gases with which the SO_2 is diluted (3 per cent. SO_2 and 3 per cent. CO_2), and it cannot be used for the manufacture of contact sulphuric acid, because the catalyst (Fe_2O_3, p. 325) becomes covered with a quantity of dust and zinc oxide; moreover, as the gases are moist, dilute sulphuric acid is obtained. The gases are often, therefore, by preference dispersed by means of very high chimneys (there is one at Boston 154 metres high) in order not to injure the surrounding vegetation. This end is, however, not always attained, and at various mines the gases are first purified in good dust chambers, and then utilised in lead chambers to make sulphuric acid of 45° to 50° Bé.

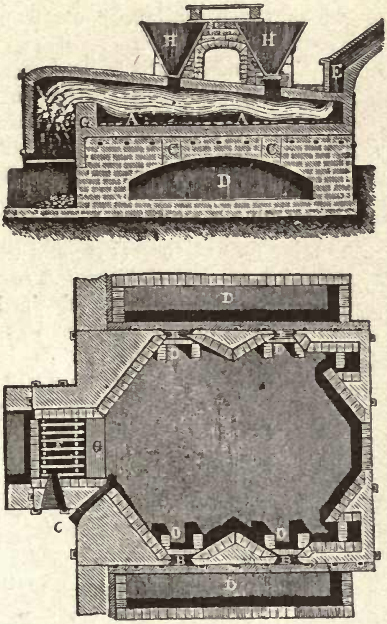


FIG. 269.

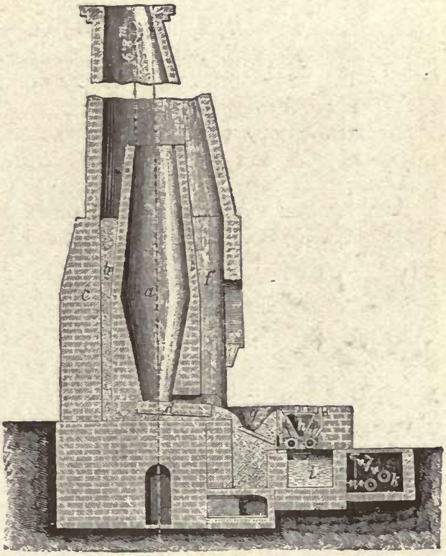


FIG. 270.

A type of cupola furnace as used at Mansfield is illustrated in section in Fig. 270. The roasted ore, which contains iron oxide and sulphides, and sulphates of copper and iron obtained by oxidation of the sulphides, is mixed with fluxes (silicates, quartz, or slag from preceding operations) and charged into the cupola, *a*. As the temperature gradually rises inside and outside (hot gases circulate in *f*) through the action of the air which passes into the cupola, a portion of the sulphur is eliminated and also any residual As and Sb. Simultaneously sulphates and oxides of copper, iron, zinc, lead, etc., are formed, and a portion of the copper sulphide remains unaltered because it is less oxidisable than the sulphides of the other metals. When the temperature is sufficiently high, a reducing action commences which is more energetic if coal has been added to the ore or if it contains bituminous matter.

The sulphates are thus converted into sulphides and the ferric oxide into ferrous oxide which separates as a slag through the action of the molten fluxes, which also dissolve many other impurities, consisting of various metals and their oxides. On the other hand, almost all the copper which was present in the state of oxide is reduced partially to metallic copper and partially to sulphide by reacting with the iron sulphide which is present: $6CuO + 4FeS = 3Cu_2S + 4FeO + SO_2$. The molten mass containing metallic copper, copper sulphide, and copper oxide mixed with other oxides and with sulphides of iron, etc., forms the so-called *coarse metal* (matte) which contains about 35 per cent. of copper. If attempts were made to produce a purer "matte" there would be a risk of copper passing into the slag. The molten mass, mixed with lighter molten slag, runs on to an inclined hearth at the base, *d*, and is discharged by two apertures, *e*, into two crucibles, *g*; the slag, which separates at the surface, overflows into the lateral receivers, *h*. The molten matte is solidified and granulated by pouring it into the vessel, *i*, in which water continually circulates through the tubes, *k*.

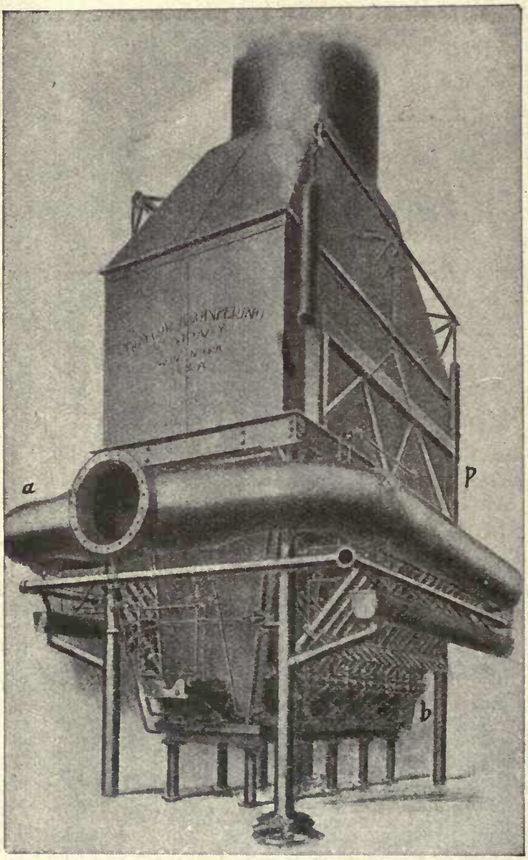


FIG. 271.

The crude matte is then concentrated and purified by submitting it once or twice to the process of roasting and melting as was done before, thus gradually eliminating the impurities by means of the slag in such a way that the greater part of the copper and the iron remains as sulphides. A concentrated matte is thus obtained, which contains much Cu_2S and FeS together with copper oxide, its total content of copper being 60 to 70 per cent. This regulus is finally treated in reverberatory furnaces where, by the direct action of the flame and of much air, the sulphides are transformed into oxides, the mass being continually stirred with iron tools by hand or suitable mechanical devices: $Cu_2S + 3O = Cu_2O + SO_2$. Furthermore a portion of the cuprous oxide is reduced to metallic copper through the action of the iron sulphide: $3Cu_2O + FeS = 6Cu + FeO + SO_2$. The iron oxide separates in the slag together with the silica remaining in the regulus and partly with silica derived from the furnace hearth. When it is certain that oxidation is complete, powdered coal is introduced into the furnace in order to reduce the metallic oxides energetically. In this manner impure *blister copper*, containing 90 to 95 per cent. of Cu, 1 to 2·5 per cent. of Fe, and 0·5 to 2·5 per cent. of sulphur, is obtained, together with a very little regulus. The slag which separates in these furnaces contains up to 1 per cent. of copper and is used as a flux in the concentration of the grey metal.

Of late years, after the work of Holloway (1879) and of Manhés (1882–1895), the treatment of grey metal is carried out directly in Bessemer converters (*see* Iron), which contain 2 to 3 tons of the regulus. In this case, contrary to the practice in the case of iron, air is blown merely over the surface of the molten mass and rapidly transforms the copper and iron sulphides into cuprous and ferrous oxides with evolution of SO_2. Cuprous oxide forms metallic copper with a portion of the Cu_2S (*see above*), whilst ferrous oxide is transformed into slag by the silica which lines the converter. 50 tons of regulus are treated in twenty-four hours and a *black copper* is obtained containing 95 to 99 per cent. of Cu, a little sulphur, and minimal quantities of other metals. The slag is re-utilised.

AMERICAN PROCESS. In cupola furnaces there are notable heat losses, high consumption of refractory materials and fuel, and not more than 20 tons of ore can be treated per twenty-four hours. By the new process of direct smelting of sulphurised or pyritic ore proposed by Holloway, the heat of combustion of the sulphur contained in the ore is partly utilised, and the process is well adapted also for poor ores. In the new type of furnace (Fig. 271) the walls of refractory material are replaced by double walls of steel, which are kept cool by a current of water, whilst the upper part of the furnace, which is of rectangular section, is built of brickwork. A large pipe, *a*, carries in the compressed air from a Root's blower at a pressure of 60 cm. of water. This is injected into the lower part of the furnace through tuyères, *b*, which may amount to 150 in number. The portion enclosed by the steel plates from *a* to *b* has a width of 0·9 metre below and 2·6 metres above and a depth of 4·3 metres. The brickwork portion below the level, *p*, up to which it is charged, has a section of 2·2 by 3 metres and is 3·3 metres high. The water which circulates between the double steel walls escapes at a temperature of 70° to 80°, and 600 to 700 cu. metres of water are used per twenty-four hours. The furnace bottom is formed of a large steel plate which can be raised in one piece for the purpose of discharging the contents. The fused regulus is discharged into suitable crucibles mounted on pivots so that they can be inverted, and these are then carried on cars directly to the Holloway-Manhès converters (Fig. 272), which differ somewhat from ordinary Bessemer converters. The furnace is charged through *p* with the ore, mixed with coke and with limestone as a flux. A portion of the fuel is sometimes replaced by pyrites or copper and sulphur, and the consumption of fuel is thus only 3 to 5 per cent. of the ore, whilst in cupola furnaces it may be as much as 20 to 25 per cent. In the converter the fused matte is transformed, by a single operation and without consumption of fuel, into crude copper by means of powerful jets of slightly compressed air which pass over the surface of the fused regulus below the molten slag and carry off the sulphur dioxide, whilst the impurities, consisting of iron, etc., which sometimes form as much as 40 per cent. of the regulus, are combined and absorbed by the quartz lining of the converter, being transformed into a fused vitreous silicate which floats on the copper and may be decanted. The quartz lining is renewed after 7 or 8 operations, and 5 to 6 converters are used for each furnace, so that time is allowed for relining, cooling, etc. Fairly pure copper (up to 98 per cent.) is obtained in the converters, but it may be refined in reverberatory furnaces as described below.[1]

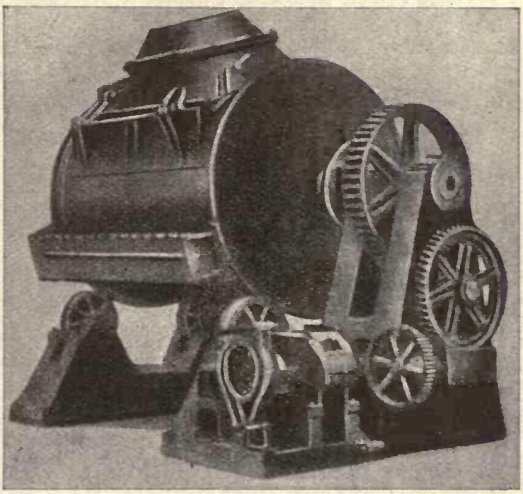


FIG. 272.

---

[1] By the Knudsen process (1907) copper may be extracted from iron pyrites containing, for example, 6·5 per cent. Cu, 33 per cent. Fe, 36 per cent. S, 16 per cent. SiO_2, and 8 per cent. Al_2O_3, by introducing the ore directly into a special furnace containing about 2 per cent. of lighted coke, an air-blast being continued for 4 to 5 hours until fusion is complete; the residual slag and matte with 50 to 55 per cent. Cu and 20 to 25 per cent. S are then discharged into a Manhès converter, where 99·5 per cent. Cu is obtained. Such a plant is working at Sulitjelma.

In 1912 the Canadian Copper Company replaced the acid linings of its converters (which last little more than 8 hours and give only 70 tons of concentrated matte) by basic magnesite linings, with which more than 4000 tons of crude matte can be worked up before renewal. In this case the siliceous slag cannot be supplied by the lining, but must be added to the matte itself. These converters are as much as 11 metres long and have a greater diameter of 3 metres; the lining of the base is 60 cm. thick and that of the walls about 40 cm. Air enters by 44 tuyères.

COPPER REFINING. The black copper may be refined in reverberatory furnaces or electrolytically. The reverberatory furnaces which are used have a small siliceous hearth, on to which the black copper is introduced and raised to a high temperature for 6 or 7 hours, all the apertures of the furnace being closed (*B*, Fig. 269). High temperatures are more easily reached in small than in large furnaces. When the mass has been thoroughly heated and melted large quantities of air are injected and a portion of the impurities, consisting of Zn, Pb, As, Sb, and S, is thus volatilised, another portion, consisting of Fe, Ni, and part of the Zn and Pb, being converted into slag by the silica of the furnace hearth. This slag floats on the melted copper and can easily be separated. Cuprous oxide, Cu_2O, is formed on the surface and penetrates into the molten metal, giving off oxygen to the copper sulphide which is still present, with evolution of SO_2.

Copper remains, which contains a little cuprous oxide, Cu_2O, and a little SO_2. In order to reduce and eliminate these products, large poles of green wood are introduced into the copper and evolve H_2O, H, CO and hydrocarbons, which stir up the mass. All the SO_2 is thus eliminated and a large portion of the Cu_2O is reduced to metallic copper. The last traces of Cu_2O are reduced by throwing powdered wood charcoal into the furnace; pure malleable and ductile copper finally remains. The reduction is more effective if a highly reducing substance is added to the fused mass, instead of green wood; such substances are copper phosphide, containing 9 per cent. of P, or manganous copper, containing 30 per cent. of Mn. Another procedure consists in pouring the copper into a bath of boron oxide, B_2O_3, which dissolves the impurities and liberates all the gases so that compact copper without blowholes results (U.S. Pat. 1,027,769, 1912). Special Bessemer converters similar to those used for steel are now sometimes used.

The electrolytic refining of copper gives a very pure product. The black copper is cast in moulds 1 metre long, 0·50 metre broad, and about 2 cm. deep, and the slabs thus obtained are subjected to electrolysis, as explained below, by using them as anodes in an electrolytic bath and depositing electrolytic copper on plates of pure copper which form the cathodes.

(2) WET TREATMENT AND UTILISATION OF BURNT CUPRIFEROUS PYRITES. This treatment is suitable for relatively poor copper ores. Burnt pyrites containing 4 to 7 per cent. of copper is treated by the wet chlorination process, whilst if it contains more than 7 per cent. of copper, dry chlorination is used, but the consumption of NaCl is then excessive, and still more so when the wet method is employed. In this case the ordinary process of oxidation which was first described is preferred.

The cupriferous pyrites which is used for the production of SO_2 in sulphuric acid manufacture is burnt in such a manner that the copper in the ash finally remains partly as cuprous oxide and partly as cuprous sulphide, Cu_2S, whilst the iron is also present as oxide and to a small extent as FeS. The product obtained under these conditions is the most suitable for dry extraction.[1]

Burnt pyrites which contains only 1 per cent. of copper is treated by the wet method. The burnt pyrites is exposed to the air and rain in heaps for some weeks and then treated in vats with dilute (Glover) sulphuric acid with stirring, or it may be passed through a number of vessels provided with false bottoms and there lixiviated systematically with dilute sulphuric acid until exhausted. The resulting liquid is discharged into other vats into which a sufficient quantity of iron turnings, or preferably of sheet iron, is placed. On stirring, a powdery reddish paste is deposited on the bottom which contains all the metallic

---

At first 60 tons of crude fused matte and 70 tons of quartz pebbles are introduced and air blown in for 45 minutes; the mass is skimmed, a further 5 to 6 tons of matte and 3 tons of quartz added, more air blown in, and so on until 70 to 80 tons of concentrated matte are obtained in the converter. The treatment of 350 tons of the matte requires air to be blown in for 30 to 50 hours. One of the advantages of these basic converters is that they yield slag poorer in copper and nickel. Flame furnaces for refining (Fig. 269) are 35 metres long and 6 metres high, the magnesite base being concave.

[1] Both Cu_2O and Cu_2S melt comparatively easily and then impede the successful combustion of the pyrites. In pyrites furnaces it is therefore inadvisable to exceed a temperature of 550° to 600° (cherry-red heat). This temperature is more easily maintained in mechanical furnaces; thus, whilst in the Maletra burners (p. 293) only about 80 per cent. of the copper remains soluble in acids, in the mechanical furnaces (p. 294), as much as 95 per cent. remains soluble. This result is obtained with more certainty if the pyrites is previously mixed with a very little sulphuric acid. Burnt pyrites containing more than 3 per cent. of copper may retain as much as 5 per cent. of sulphur.

copper and forms the so-called *cementation copper*, which contains 60 to 70 per cent. of copper when moist, and 75 to 80 per cent. when dry.

This cementation copper is ordinarily used for the preparation of crystallised copper sulphate (*which see*) or is treated as a rich ore for the extraction of copper by the usual processes. 400,000 tons of cupriferous pyrites are used annually in England.

(*a*) **DRY CHLORINATION PROCESS.** The sulphur contained in the burnt pyrites should if possible be present in smaller quantity than the copper and not in larger quantity, because in that case more salt is required and the roasting takes more time. The powdered cupriferous residues are mixed with 10 to 15 per cent. of sodium chloride and heated for 10 to 15 hours in reverberatory or preferably in muffle furnaces, as the temperature is more easily regulated in the latter. This should not exceed 500° (below red heat), as otherwise the cupric chloride forms volatile cuprous chloride, which is lost. In certain cases it is advisable to add 6 to 7 per cent. of ferrous sulphate (for each 4 to 5 per cent. of copper), as time is thus gained in roasting and copper sulphate is more easily formed, and this transformed on heating into chloride by the action of the sodium chloride.

In order to determine whether the roasting is completed, a portion of the mixture is removed from the furnace with a ladle, washed with water and then with dilute hydrochloric acid, and copper is tested for in the residue by boiling it with aqua regia, and then dissolving in ammonia. According to the more or less intense blue colour of the solution, the quantity of copper which has not been attacked by the sodium chloride through insufficient roasting is estimated. The roasted product is systematically lixiviated with water in vats similar to those used for soda (p. 593), the mother-liquors from a previous treatment being utilised. The solution of copper salts, after filtration or decantation, is exposed to so-called *cementation* in wooden or cement vats, the copper being precipitated by iron filings or preferably by iron turnings, sheet iron, or, better still, spongy iron, with continual stirring and heating to 50° to 60° with a jet of steam. Theoretically 88 parts of iron precipitate 100 parts of copper, but in practice it is necessary to employ at least 200 parts of iron. Sometimes treatment with SO_2 is resorted to in order to obtain a purer cementation copper; thus obtained it contains from 60 to 85 per cent. of copper, the rest consisting of iron salts and other impurities.

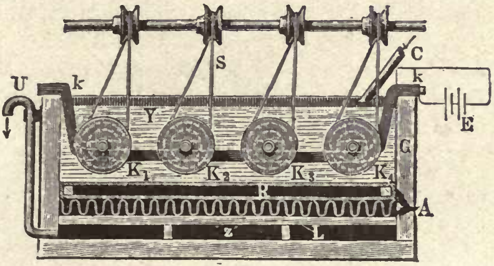


FIG. 273.

(*b*) **WET CHLORINATION.** Burnt pyrites is treated with a solution containing 1000 parts of water, 280 parts of ferrous sulphate, and 120 parts of sodium chloride, at 80°, the whole being then stirred for three or four days. Ferrous chloride is thus formed, and this transforms the copper oxide into a mixture of soluble cupric chloride and insoluble cuprous chloride: $3CuO + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2$. On adding iron filings, or preferably iron turnings or spongy iron, to this mixture, free copper (cementation copper) is precipitated and ferric chloride is formed which is converted into ferrous chloride by excess of iron: $2CuCl_2 + Cu_2Cl_2 + 2Fe = Fe_2Cl_6 + 4Cu$.

The solution of ferrous chloride is used for the treatment of fresh burnt pyrites instead of sodium chloride. The cementation copper is used for the preparation of refined copper or copper sulphate.

(3) **ELECTROLYTIC PROCESS.** At one time only rich ores or the black copper obtained on treatment of the ore (*see above*) were treated by this process. To-day, however, poor ores, especially when they contain sulphur, are also treated by the Siemens-Halske process, which uses a solution of ferric sulphate, or by the Höpfner process, in which a solution of cuprous chloride is used. Siemens and Halske treat the powdered ore or cupriferous iron pyrites, which has been slightly roasted, with a solution of ferric sulphate containing a little H_2SO_4, in order to increase its conductivity. The copper of the ore passes into solution, forming copper sulphate and reducing the ferric sulphate to ferrous sulphate: $Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$. This solution is electrolysed in a continuous apparatus, which is shown diagrammatically in Fig. 273. There is a wooden

vat, *G*, containing a perforated false bottom, *L*, on which a series of carbon anodes, *A*, rest. These are covered by a layer of filtering material, *R* (felt or other material), which separates the anode compartment from the upper cathode compartment. In the latter, which is filled with the solution, a series of cylinders, K_1 to K_4, clad with sheet copper are immersed. These are united with one another and connected to the negative pole, *K*, and are rotated by the belts, *S*, in such a manner that the bath is continuously stirred. When a current is passed copper is deposited on the cathodes, *K*, whilst SO_4 ions are formed at the anodes which oxidise the ferrous sulphate formed in the cathodic compartments; this then passes to the anode through the filter, *R*: $CuSO_4 + 2FeSO_4 = Cu + Fe_2(SO_4)_3$. The solution, almost free from copper and containing regenerated ferric sulphate, escapes through the syphon tube, *U*, and is used to dissolve fresh copper in the vat in which the ore is treated; it is then again passed through the electrolytic apparatus, the process being continuous. After various modifications the Siemens-Halske process is now arranged as indicated schematically in Fig. 274. *A* is a vat containing a solution of copper sulphate and ferrous sulphate. This solution passes through the tube *B* into the cathodic compartment, *C* and *K*, and after having deposited the greater portion of the copper, passes into the anodic compartment, *a*, where it is oxidised, forming ferric sulphate. The ore is crushed in *E*, and the powdered ore passes along the channel, *F*, into the vat *H*, which is provided with a stirrer. The oxidised solution, containing little $CuSO_4$ and much $Fe_2(SO_4)_3$, also passes into this vat through the tubes *D* and *G*. In contact with the powdered ore, a solution of $CuSO_4$ and $FeSO_4$ is formed, and the extracted ore is then deposited in *K*, whilst the liquid passes into the vat *A* through the tube *M*. A current density of 16 amps. per square metre is employed at an E.M.F. of 0·7 volt. Ores containing up to 0·1 per cent. of copper can be extracted in 10 hours.

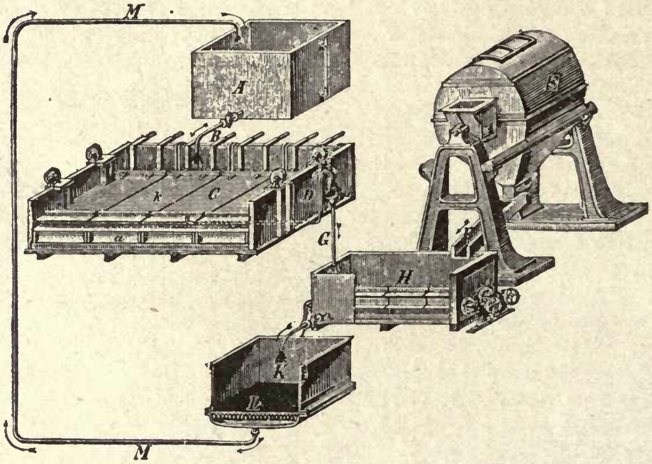


FIG. 274.

By the Höpfner process the copper is dissolved in a solution of cuprous chloride instead of one of ferric sulphate.

Another electrolytic process which has yielded good practical results after many improvements is that of Marchese, who uses the matte $Cu_2S + FeS$ as anodes. This regulus is obtained in the initial treatment of the ore (*see above*). The bath consists of a solution of the ore in H_2SO_4 and the cathode of plates of pure copper on which the new copper, which is very pure (99·8 per cent.), is deposited, whilst sulphur is deposited at the anode.

In general the electrolytic precipitation of copper from acid solution is incomplete if nitric acid is present, but it becomes complete in presence of urea.

Certain impurities, especially arsenic and antimony, render difficult the deposition of copper in a compact, homogeneous and pure condition. This inconvenience, even in presence of 4 to 6 per cent. As, is obviated by heating the bath to 40°, whilst addition of NaCl, gelatine, gum or tannin (not of peptones) facilitates the deposition.

In 1909 280,000 tons of copper were refined electrolytically throughout the world, and in 1912 more than 730,000 tons, mostly in the United States, where crude 96 to 99 per cent. copper is used, and the solutions electrolysed contain 12 to 24 per cent. of copper sulphate in presence of 4 to 10 per cent. of free sulphuric acid and minimal proportions of hydrochloric acid to precipitate the small amount of silver dissolved. The solution is kept at 40° to 60° by continuous circulation, a current of 12 to 15 amps. (at 0·1 to 0·3 volt.) per sq. ft. being used; 1 ampère gives 28·5 grams of Cu per 24 hours.

PROPERTIES. Pure metallic copper has a beautiful bright red and lustrous colour. It is fairly hard (*see* Table, p. 514), but also fairly ductile and flexible, and may be obtained in wires and in very thin foil, which has a green appearance by transmitted light. Its specific gravity is 8·94; it melts at 1085° and solidifies to an irregular mass, so that it is difficult to cast. At temperatures near its melting-point it is brittle and can be powdered. It is a good conductor of heat and electricity (*see* Table, p. 514) and minimal traces of impurities, recognisable micrographically (*see* p. 515 and chapter on Iron), exert an appreciable influence on the electrical conductivity; for pure copper this is 99·59 (silver = 100), while if 0·0042 per cent. of Sb, As and Pb is present, it rises to 100·3, and with 0·00074 per cent. Bi it falls to 98·5. Copper wire prepared directly from electrolytic copper has the conductivity 103, since it is very pure and is more compact in structure than fused copper. It keeps well in dry air, but in presence of moisture becomes covered with a green layer of the basic carbonate, **Verdigris.** When heated in the air it is readily transformed into the black oxide, CuO. It is not appreciably dissolved by HCl or H_2SO_4, although in presence of air, or in the form of oxide, copper is attacked more easily by these two acids. On heating with strong H_2SO_4, SO_2 is evolved and $CuSO_4$ is formed. Dilute nitric acid dissolves it even in the cold with evolution of NO. Zinc, iron, magnesium, etc., separate it from solutions of its salts in the metallic state. When heated with SO_2 under pressure solutions of $CuSO_4$ form a precipitate of pure copper. Ammonia dissolves copper in presence of air, forming an intensely blue solution of **Hydroxyammoniate of Copper.** Certain vegetable organisms are extremely sensitive to the poisonous action of copper and its salts.

APPLICATIONS. Much copper, in the very pure form in which it is obtained to-day by electrolytic processes, is used in electric installations as a good conductor of the current. It is also used in the construction of much industrial machinery, for cooking utensils, for engraving, etc., but the greater portion of the copper which is used goes to form alloys with other metals.

ALLOYS OF COPPER. We shall enumerate the principal alloys of this metal. *Brass* contains 3 parts of Cu and 1 part of Zn, and has a yellow colour. The proportion of zinc may vary somewhat, but is never below 18 per cent. It is used for many mechanical purposes, because it is harder and less oxidisable than copper. It sometimes contains 1 to 2 per cent. of lead, and may then be readily turned. Brass is ductile and malleable, but becomes brittle when hot, although this is not the case when 60 per cent. of copper is present. For casting artistic objects as much as 3 per cent. of tin may be added. Among the numerous varieties of brass is *Delta metal,* which has the colour of gold, is almost unoxidisable and somewhat elastic, and is used in art castings and for mechanical and naval construction; it contains 54 to 56 per cent. Cu, 40 to 42 per cent. Zn, about 1 per cent. Fe, and small proportions of various other metals (*e. g.*, 1·3 per cent. Mn, 1·8 per cent. Pb, besides Sn, Al, P, Ni, etc.). In the condensers of marine steam engines use is made of a series of brass tubes (*e. g.*, 70 Cu, 1 Sn, and 29 Zn), which easily corrode for some reason not clearly known (stray electric currents, contact with electronegative bodies, presence of tin in the alloy, etc., etc.); the corrosion is, however, notably diminished if the tubes are covered with an electro-positive metal (Zn, Al, etc.), and especially if the tubes are arranged vertically so as to avoid incrustation, which is especially injurious when separated from water softened with lime and sodium carbonate. *Bronze* is an alloy of copper and tin, and sometimes contains a little zinc and lead. *Bell metal* contains 75 to 80 per cent. of copper and 20 to 25 per cent. of tin; it sometimes contains also traces of Zn and Pb. It has a greyish-yellow colour, is easily melted, has a fine granular structure, is hard, brittle, and very sonorous. *Gun metal* contains 89 to 91 per cent. of Cu, 9 to 11 per cent. of Sn, and sometimes 1 to 1·5 per cent. of Zn. *Phosphor-bronze* is obtained from ordinary bronze by the addition of 0·5 to 0·8 per cent. of phosphorus (in rare instances and for special purposes up to 3 per cent. of phosphorus, which is added in the form of an alloy of phosphorus and copper or phosphorus and zinc); phosphor-bronze is harder than ordinary bronze and is suitable for objects which are exposed to tension, for example, the wires in electric cables, etc. The phosphorus combines with the oxygen contained in the metal. When it contains 3 per cent. of phosphorus it costs one-third more than that containing only 0·5 per cent. of P. *Statuary bronze* contains up to 5 per cent. of zinc and 2 per cent. of lead. It can be worked with the chisel, and is suitable for artistic objects, because when cast it readily reproduces every detail and has the property of becoming readily covered with a greenish layer which renders it similar to antique bronze.[1] *German silver, pakfong,* or *pinchbeck* is an alloy of Cu, Zn, and Ni in varying proportions (for example, 60 per cent. of Cu + 24 per cent. of Zn + 16 per cent. of Ni), and according to the varieties manufactured by the firm of Krupp it is considered to be of first quality when it contains about 17 per cent. of Ni, of second quality with 12 per cent., of third quality with 8 per cent., and of fourth quality with less than 5 per cent. It has an almost silvery-white colour, and is harder and more resistant to chemical reagents than brass. Objects made of this alloy and coated with silver are called *Christofle* (the name of the French maker). *Silico-bronze* contains small and varying quantities of silicon, which acts in a similar manner to phosphorus and renders the coefficient of expansion of the metal smaller, although it still remains a good conductor of electricity, so that it is very suitable for the production of telegraph and telephone wires. *Manganese bronze* contains up to 30 per cent. of Mn, which combines with oxygen in a similar manner to phosphorus and may replace a considerable portion of the tin; it is very hard and tenacious and is well suited for the construction of the screws of vessels. There are also bronzes containing aluminium, tungsten, etc.

STATISTICS AND PRICES. The production of copper in different countries and at different times is shown in the following table [2] (tons):

---

[1] **Coloration of Metals and Alloys.** A superficial black coloration is often given to bronze and brass, this being obtainable as follows: Ammonia solution is neutralised with copper carbonate and the latter then added in slight excess so that it does not completely dissolve. The brass objects are immersed for some minutes in this solution at 50° to 60°, and thus acquire the black colour. Another process consists in heating the brass or copper article to 120° and immediately pouring over it a solution composed of 3 parts of water, 2 of saturated cupric nitrate solution, and 1 of saturated silver nitrate solution; the brownish-black coloration thus obtained becomes black if the object is immersed in liver of sulphur solution (*see* p. 544). According to another method, the article is immersed in a solution containing 5 per cent. of NaOH and 1 per cent. of potassium persulphate at 100°; when evolution of oxygen ceases, a further 1 per cent. of the persulphate is added.

[2] For Italy the amounts of copper produced, imported, and exported are as follows (tons):

		1910	1911	1912	1913	1914	1915	1916	1917
Production	(*a*) Block copper, etc.	1,766	1,666	2,319	—	1,839	—	—	—
	(*b*) Alloys, sheet, wires, tubes	20,701	21,242	24,340	24,625	20,464	—	—	—
Imports	(*a*)	21,566	28,510	33,630	30,280	22,719	51,057	58,727	74,320
	(*b*)	8,759	10,131	9,853	6,368	9,820	3,665	9,639	18,795
Exports	(*a*)	837	743	1,717	1,465	684	173	167	47
	(*b*)	919	566	687	931	189	108	304	66

In 1911 England imported 166,000 tons of copper and exported 75,000 tons, and in 1915 imported 228,000 tons, and exported 38,000 tons.

Spain's production was:

			£
Cementation copper	1915	12,374 tons for	531,476
	1916	11,233 ,, ,,	964,394
Blister copper	1915	19,058 ,, ,,	1,417,915
	1916	17,507 ,, ,,	2,147,023
Block copper	1915	1,767 ,, ,,	96,282
	1916	1,762 ,, ,,	255,495
Copper wire	1915	1,500 ,, ,,	180,000
	1916	1,500 ,, ,,	180,000

In the United States most of the copper is made in Montana (150,000 tons in 1912), Arizona 175,000 tons), Michigan (110,000), Utah (66,000), California (14,000), Nevada (40,000), and

	1905	1909	1911	1912	1913	1916
United States . .	412,000	528,000	518,700	592,400	556,000	880,880
Japan . . .	36,500	47,800	55,000	67,000	73,100	90,000
Chili . . .	29,600	36,400	—	—	39,400	66,500
Mexico . .	10,300	12,500	—	—	58,300	55,100
Canada . . .	20,900	24,500	—	—	—	—
Spain (and Portugal)	45,500	53,000	18,300	23,300	54,600	50,000
Germany . .	31,700	31,000	37,500	39,800	25,300	35,000
Australia . .	34,500	47,800	40,000	44,900	47,300	35,000
Russia . .	8,800	18,500	25,600	33,500	34,300	16,000
England . .	67,900	66,000	67,700	63,200	52,100	—
France . .	7,600	7,500	—	—	12,000	—
Whole world .	692,000	853,000	875,000	—	1,005,000	—

The consumption of copper in different countries is as follows (tons):

	1903	1910	1912	1913	1914
Germany . .	120,000 (?)	200,000	231,700	259,300	265,000
England . . .	108,000	146,000	144,700	140,300	147,000
France . . .	50,000	80,700	98,500	103,600	107,000
Austria-Hungary .	19,000	33,500	48,200	39,200	41,000
Russia . . .	18,000	28,600	40,000	40,200	41,000
Italy . . .	—	23,200	34,200	31,200	30,900
Belgium . . .	—	13,000	15,000	15,000	15,000
Holland . . .	—	1,000	1,000	1,000	1,000
Rest of Europe .	—	7,600	10,200	13,300	3,000
United States . .	—	338,700	371,800	348,100	342,500
Rest of America .	—	3,000	3,000	3,000	3,000
Asia, Australia, Africa	—	19,800	40,400	50,300	40,000
Whole world .	727,400	894,900	1,038,700	1,044,500	1,031,400

Prices are referred to the "Lake" brand of copper valued at New York or to the "Standard" brand of London (dearer than the Mansfield), but the variations are almost always due to financial speculation or to American over-production. The mean price of refined copper was £56 per ton in 1890, £44 in 1895, £76 in 1900, £71 in 1905, £89 in 1907, and £60 in 1909, and then increased in 1910 and fell again in 1911 owing to diminished American consumption. In 1913 it rose again to £76.

In order to prevent rapid changes in price, an attempt was made in 1907 to constitute an international trust to regulate and diminish production, but this failed, although it was later taken up again secretly and apparently led to agreement in 1910.

The price of copper rose to fantastic figures during the European War. Thus in Italy smelting copper cost £290 per ton in July 1917 and £310 in July 1918, when bar copper cost £510, whilst in America in December 1916 the market price was £132.

Alaska (15,000 tons). The United States gave 80 per cent. of the world's production and in 1911 exported 346,000 tons of copper. The copper refineries of the United States had an annual capacity of 762,000 tons in 1914 and 1,270,000 tons in 1918, that of the Guggenheim Company being 550,000 tons and that of the Anaconda Company 320,000.

Before the European War the production in Russia was continually increasing, especially in the Urals, where in 1912 18,000 tons were made, while in the Caucasus 10,000 tons and in Siberia 5000 tons were produced. Owing to the high consumption of electrolytic copper (17,000 tons) Russia continues to import copper (7000 tons in 1912), the production of electrolytic copper at the same time increasing rapidly.

Japan consumed about 32,000 tons of copper and China about 5000 tons in 1914.

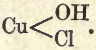
In Chili a large works was started in 1914 at Chuquicamata (Antofagasta province) to treat 10,000 tons of poor copper ore (2 per cent. Cu) from the Lampera deposits, which probably contain 200,000,000 tons of ore. This is lixiviated with dilute sulphuric acid, and the chlorides are separated from the solution by passing the latter into tube mills with empty copper balls, on which cuprous chloride forms. The clear solution is electrolysed with sheet copper anodes and magnetite cathodes (Griesheim-Elektron type). About 91 per cent. of the copper of the ore is thus obtained.

The price of brass in round rods or in sheets was £72 per ton in 1909, but during the European War it rose in Italy to £300 in July 1917 and to £520 in July 1918.

CUPROUS COMPOUNDS

CUPROUS OXIDE : Cu_2O. This is found in nature as *cuprite* in red regular octahedra, and is obtained by reducing cupric salts in the hot, whilst in the cold yellow cuprous hydroxide, $Cu_2(OH)_2$, is formed. Thus cuprous oxide may be produced with an alkaline solution of grape sugar, which contains an aldehydic reducing group, or with arsenious acid. It is a red substance of sp. gr. 5·35, which is not attacked by the air in the cold. It dissolves in ammonia and then acquires a blue colour in contact with the air. In presence of sulphuric acid it forms copper and copper sulphate,

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$

CUPROUS CHLORIDE: $CuCl$ or Cu_2Cl_2. This compound is formed on burning copper in an atmosphere of chlorine or on boiling cupric chloride solution with copper and HCl, or by reducing a solution of copper sulphate in a current of SO_2 in presence of sodium chloride. It then separates as a white powder on pouring the solution into water, but in contact with air it acquires a green colour through the formation of copper hydroxychloride :  $Cu<^{OH}_{Cl}$.

It melts at 430°, distils unaltered at 1000°, and has a vapour density corresponding with the formula Cu_2Cl_2. With HCl or NH_3 solutions a colourless solution is first obtained which rapidly becomes blue in the air with formation of cupric compounds and rapidly absorbs carbon monoxide with formation of $2CuCl,CO,2H_2O$, which separates in colourless crystals.

Cuprous Bromide and **Iodide** are more insoluble in water than the chloride. On adding KI to a solution of copper sulphate, cuprous iodide is formed, and half the iodine is liberated, $2CuSO_4 + 4KI = 2SO_4K_2 + 2CuI + I_2$.

CUPROUS CYANIDE : $CuCN$. On adding potassium cyanide to a solution of copper sulphate, cuprous cyanide is first separated, but this immediately dissolves in an excess of KCN, as it is completely transformed into a double salt, Cu_2Cy_2, 2KCy (the symbol Cy represents the monovalent cyanogen group, CN). This salt no longer shows any reaction for copper as it is dissociated in solution into the anion $(Cu_2Cy_4)''$, and the cations, $2K^{\cdot}$.

A **Cuprous hydride, Cu_2H_2,** is also known, and is formed as a yellow powder which then turns brown on heating copper sulphate solution with a solution of hypophosphorous acid. It reacts with HCl according to the following equation :

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

CUPROUS SULPHIDE : Cu_2S. This compound is found in nature as *chalcosine* in trimetric crystals, and is formed on burning copper in sulphur vapour or on heating cupric sulphide in a current of hydrogen.

CUPRIC COMPOUNDS

COPPER OXIDE, CUPRIC OXIDE : CuO. This oxide is a black powder which is obtained by heating copper strongly in the air, or by heating the hydroxide, carbonate, or preferably the nitrate of copper, to redness. When heated it readily gives off oxygen to organic matter in contact with it, burning it completely and being reduced to metallic copper, the carbon of the organic matter being converted into CO_2 and its hydrogen into H_2O. For this reason it is used in the analysis of almost all organic substances. The crude product costs £90 per ton, when pure £150, and when pure for analysis 5*s*. 7*d*. per kilo. Italy produced 10·5 tons in 1908, of the value of £336.

COPPER HYDROXIDE : $Cu(OH)_2$. On treating the solution of a copper salt with NaOH, a voluminous bluish-green precipitate of $Cu(OH)_2$ is formed which becomes brown and finally black on heating, as it is transformed into CuO. Its solution in NH_3 is intensely blue and has the property of dissolving cellulose; it is called *Schweitzer's reagent.*

$Cu(OH)_2$ only dissolves in NaOH in presence of certain organic substances, such as tartaric acid, sugar, etc. It costs a little more than the oxide.

CUPRIC CHLORIDE : $CuCl_2$. This compound is formed on dissolving copper carbonate or oxide in HCl. It crystallises from water in greenish needles with $2H_2O$, whilst when anhydrous it has a yellowish-brown colour and melts at 60°, being then transformed into $Cu_2Cl_2 + Cl_2$. It is soluble also in alcohol. The concentrated aqueous solution is green because it is only slightly dissociated, whilst on diluting with much water it becomes blue because of the presence of blue $Cu^{\cdot\cdot}$ ions, whilst the undissociated $CuCl_2$ molecules are yellowish-brown, which explains the green colour of the concentrated solution, this consisting of a mixture of non-dissociated $CuCl_2$ and $Cu^{\cdot\cdot}$. The latter ion is always blue in all cupric compounds.

It forms well-crystallised double salts with HCl and NH_4Cl.

Cupric Bromide is similar to the chloride. **Cupric iodide** is not known, because it dissociates into $I_2 + Cu_2I_2$ as soon as it is formed.

COPPER NITRATE : $Cu(NO_3)_2$. This is prepared by dissolving Cu or CuO in nitric acid. It is very soluble in water and forms deep blue crystals with 4 or $6H_2O$. It is also soluble in alcohol and forms CuO on heating to redness.

BASIC COPPER CARBONATE. The neutral carbonate is not known, but the basic carbonate exists in two forms as minerals, *Malachite*, $CuCO_3,Cu(OH)_2,\frac{1}{2}H_2O$, and *Azurite*, $2CuCO_3,Cu(OH)_2$.

COPPER SULPHATE, BLUE VITRIOL : $CuSO_4$. This is the most widely used copper salt. It is very stable and is obtained by dissolving copper and many copper minerals in hot, dilute sulphuric acid in contact with the air. It is necessary, however, to remember that except in the presence of much air copper reacts scarcely or not at all with sulphuric acid (*see* p. 523), and it is therefore preferable in such cases to start from copper oxide. For preparing the sulphate industrially a lead tower is sometimes used, filled with copper turnings, down which a spray of dilute sulphuric acid descends to be discharged at the base and repeatedly pumped to the top of the tower. When the reaction between the acid and the copper first starts, heat is produced, which causes a strong current of air to be drawn in through an aperture at the base of the tower. This becomes heated and escapes at the top after having oxidised the copper and thus facilitated its transformation into sulphate. The sulphate is also prepared by lightly roasting copper sulphide in the air and then extracting the resulting copper sulphate with water, from which it crystallises in blue triclinic crystals containing $5H_2O$. This is the ordinary *blue vitriol*, which effloresces superficially in the air owing to the loss of a little water. At 100° it loses $4H_2O$, but loses the final molecule of water only at 200°, leaving a white powder of anhydrous copper sulphate which is somewhat hygroscopic, and is used for dehydrating various substances, when it regains its blue colour. 100 parts of water at 20° dissolve 42·3 parts of $CuSO_4,5H_2O$, and the solution has an acid reaction in common with those of many salts of heavy metals which are hydrolytically dissociated by water. Copper sulphate has various practical applications and is therefore manufactured on a large scale by one of the following industrial processes.

Cupriferous pyrites is now often used after it has been employed for the preparation of SO_2 in sulphuric acid manufacture, and is treated in the manner already described for the preparation of copper, that is, cementation copper is prepared from it, which is then used for the manufacture of the sulphate. It is found in practice that much burnt cupriferous pyrites cannot be extracted very easily with water and H_2SO_4, because at the temperature of the pyrites burners (up to 750°) the sulphate and sulphide of copper which are first formed give rise to the oxide and to a regulus which renders it difficult to recover the copper except by the process of chlorination.

In order to prevent a considerable portion of the copper sulphate formed in the pyrites burners from decomposing through the employment of too high a temperature, it has been proposed (Gianoli, *Industria*, 1903, p. 731) to mix the pyrites before roasting with about 10 per cent. of sodium bisulphate or sulphate. The lixiviation of the burnt pyrites is conducted in the usual manner with water and sulphuric acid, and the copper is then much more completely extracted. Copper is separated from the solution by cementation with iron (*see above*).

The cementation or granulated copper obtained by any method is placed in lead-lined wooden vats. Crude sulphuric acid is added and the whole is diluted with mother-liquors from a previous crystallisation of copper sulphate until a density of about 29° Bé. is acquired, after which the whole is heated to 85° to 90°. It is necessary to aërate the liquid well, as otherwise the copper sulphate which is formed is partially transformed into cuprous sulphate in presence of free copper, and it is necessary to oxidise this with air in order to transform it into cupric sulphate again. The injection of air and the necessary heating can be obtained simultaneously by employing a steam injector. In certain cases it is convenient to heat and oxidise the cementation copper by spreading it out in a reverberatory furnace, carefully regulating the temperature and the current of air and stirring the material so that the copper is almost entirely converted into the black oxide. This then forms copper sulphate on simple solution in sulphuric acid. The aqueous solution of the sulphate should be almost neutral (otherwise copper oxide is added), and is concentrated in large shallow leaden pans (3 × 3 × 0·55 metres), which rest on iron plates under which the hot gases from a furnace circulate in flues. After a certain concentration has been acquired, crude copper sulphate separates abundantly on cooling. This is then redissolved in mother-liquors obtained from pure copper sulphate and previously diluted with water to 14° to 15° Bé.; a solution of crude copper sulphate of a concentration of 26° Bé. when hot is thus obtained. If a more concentrated or saturated solution were employed very small and impure crystals would be obtained. The liquid is then heated until it is completely clarified, and the solution is thus slightly concentrated. It is then poured into the crystallising boxes, which are lined with lead (3 metres × 1·5 metre × 1 metre deep) or copper and in which large copper wires are suspended, the sulphate collecting on these in bunches of large crystals. According to an American process which has also been applied in certain Italian works (Rifredi) the copper is heated to its melting-point and then poured in a thin stream into water in order to enable it to be easily oxidised and attacked by the sulphuric acid. Small, thin, hollow spheres are thus obtained (although it is necessary to employ very pure copper in order that this may occur), which are placed in a lead-lined cylinder some metres high, down which a spray of sulphuric acid of 28° Bé. is then poured from above, whilst a current of air ascends from below. When the liquid reaches the base it consists of a hot saturated solution of copper sulphate, ready for crystallisation (if not almost neutral, a little oxidised copper is added). The mother-liquors from this crystallisation are again pumped to the top of the cylinder, which is always kept filled with new copper spheres, and is continually fed with sulphuric acid in such a manner as to obtain a solution of copper sulphate of constant concentration. When pure copper is being treated, the mother-liquors may be continuously re-utilised. The crystallisation lasts from 8 to 12 days, and occurs on the walls and floor, or on leaden strips introduced into the solution. The crystals form best if the liquid contains a little free sulphuric acid, and this amount is regulated by the workmen themselves, who mix a given volume in a test-tube with a very dilute solution of alkali of fixed strength until neutralisation occurs, when a precipitate of copper hydroxide just commences to be formed. By making two tests with varying quantities of alkali, the workmen easily control the limit of acidity. In some places the crystals are separated from the mother-liquor in a hydro-extractor, but many of the crystals are thus broken and lose their commercial value. They are therefore usually spread on trays with raised rims and allowed to dry in the air in large chambers, which are well ventilated in summer or gently heated in winter (to 25° to 30°). Into these drying chambers much light should not be admitted, and care must be taken that the crystals are not dried too much, or they lose their clearness. One kilo of copper theoretically produces 3·934 kilos of $CuSO_4,5H_2O$. The mother-liquors are used in the treatment of the raw material, as was explained above.

According to Gin's process (International Congress of Applied Chemistry at Berlin, 1903) copper sulphate may be profitably prepared by lightly roasting ores containing copper and iron in such a way that a large portion of these metals is obtained in the form of sulphates. These are then extracted with water and a current of SO_2 passed into the solution to reduce the ferric sulphate to ferrous sulphate. The whole is then heated in autoclaves to 180°. At this temperature the ferrous sulphate separates from solution, whilst copper sulphate remains dissolved and is easily separated from the iron by straining or centrifuging. According to U.S. Pat. 875,012 of 1907 burnt pyrites is treated with dilute sulphuric acid and 2 to 5 per cent. of calcium hypochlorite; the whole is then heated to 70° to 80° for 12 to 24 hours, in which manner the copper only is dissolved and not the iron.

APPLICATIONS AND STATISTICS. Copper sulphate is used for copper-plating, in dyeing and printing, in the manufacture of pigments containing copper powder, for preserving wood and hides, and in considerable quantities in wine culture as a remedy for *Peronospora*.[1] The price varies with the price of copper, and was about £20 per ton in 1904, then rose to £26 in 1906 to 1907, and dropped after 1907 to below £18 per ton, rising again to £20 per ton in 1910 and to £24 in 1912. During the European War the price rose in Italy to £120 per ton, but in 1916 the Government fixed the price at £56 and in 1917 at £88.

In France the price was controlled in 1917 at £64 per ton for copper sulphate produced in the country and at £78 for the imported sulphate.

In 1900 the world's production was 100,000 tons, in 1912 203,860, and in 1913 178,785 tons.[2]

COPPER SULPHIDE : CuS. This compound is obtained as a black precipitate on passing a current of H_2S into a solution of a copper salt, even in presence of acid. It is insoluble in water and in dilute acids. When exposed to moist air it is slowly converted into sulphate; on the other hand, when heated in a current of hydrogen it is transformed into cuprous sulphide. A theoretical explanation of the fact that certain metals are completely precipitated by H_2S from acid solution, whilst under the same conditions others are not precipitated, may be deduced from the study of electrolytic dissociation. In the case of copper sulphide the reaction only occurs between the ions of copper sulphate, which is almost completely dissociated into $Cu^{\cdot\cdot}$ and SO_4'', and the few free $H^{\cdot}$ and S'' ions. The

---

[1] *Peronospora viticola* (mildew) is a microscopic fungus developing especially on the leaves of the vine; it appears as spots of mould on the under-surface of the leaf and causes drying as well as diminution or destruction of the crop of grapes. It is combated by sprinkling the leaves several times in summer with copper sulphate solution rendered basic by means of calcium hydroxide (*Bordeaux mixture*): 1 kilo of copper sulphate in 100 litres of water, 0·5 kilo of slaked lime being added. In Italy the Electrochemical Company of Caffaro (Brescia), in order to utilise electrolytic chlorine, prepared the so-called *Caffaro paste*, which contains especially copper oxychloride (16·5 per cent. Cu, 8·4 per cent. Ca, 17·5 per cent. Cl, 3·6 per cent. combined oxygen, and 53 per cent. of water and loss on ignition); when mixed with 100 parts of water it may be used instead of Bordeaux mixture, and also against potato disease and various other cryptogamic diseases of the tomato and fruit-trees.

[2] The figures for Italy are as follows (tons):

	1900	1905	1910	1911	1912	1913	1914	1915	1916	1917
Production . .	13,191	26,212	36,236	35,000	52,312	44,497	31,302	41,272	48,000	—
Importation . .	31,000	30,684	13,582	37,876	36,567	30,450	21,906	14,080	6,098	231
Exportation . .	—	—	670	106	1,387	522	1,814	6	5	53

Germany produced 7000 tons of copper sulphate in 1905, 5209 in 1910, and 5682 in 1913, and imported 2200 tons in 1905, 5080 in 1908, 6550 in 1909, and 7074 in 1912; about 4000 tons are exported per annum.

Austria-Hungary produced 11,800 tons in 1910 and 15,400 in 1913, and imported also 4,000 tons in 1909, 6600 in 1911, and 16,132 in 1912.

France consumes on an average 50,000 to 60,000 (40,000 prior to 1910) tons of copper sulphate per year, and since the production fell in 1915 to 16,000 tons (whereas from 1908 to 1913 it had been 28,000 tons annually) and rose to 27,000 tons in 1916, France has always had to import copper sulphate (12,000 tons in 1909, 16,800 in 1912, 24,000 in 1914, 33,868 in 1915, and 20,933 in 1916), mostly from England. For 1917 the expected production, divided between five or six factories, was 48,000 tons. France exported 5812 tons in 1913, 6067 in 1914, 3886 in 1915, and 4818 in 1916.

Spain produced 1,127 tons in 1915 and 17,600 in 1916, whereas formerly it did not produce copper sulphate and imported about 6000 tons per annum.

England exported 72,432 tons in 1908, 44,330 in 1909, 81,111 (£1,520,000) in 1911, 85,461 in 1912, 76,847 in 1913, 69,000 in 1914, 66,257 in 1915, and 39,435 in 1916. The output of copper sulphate in England corresponds with the exportation, the amount used being negligible.

The United States produced 12,400 tons in 1910, 15,200 in 1911, 18,000 in 1912, 24,644 in 1913, 14,414 in 1914, 18,600 in 1915, and 5910 in 1916. The exports were 3366 tons in 1911, 1891 in 1913, 6322 in 1915, and 8846 in 1916.

copper sulphide, CuS, which results, is very insoluble and is deposited, but as fast as the $Cu^{\cdot\cdot}$ and S'' ions are eliminated, the equilibrium which first existed between the H_2S ions and its undissociated molecules is disturbed. A further portion of the H_2S molecules then dissociates into the corresponding ions, and these unite with further $Cu^{\cdot\cdot}$ ions, forming fresh copper sulphide which separates, and the reaction thus continues until the copper is completely precipitated in the form of CuS, so long as the solution of copper sulphate is sufficiently dilute to permit of its complete dissociation : $CuSO_4 + H_2S = CuS + H_2SO_4$. If, however, a strong, free, dissociated acid is present, the new $H^{\cdot}$ ions will hinder the ionisation of the H_2S and no precipitate of copper sulphide will then be formed.

We may also explain the laws which regulate the equilibrium of any given reaction and the conditions under which a precipitate in general can be formed by certain general considerations. This copper sulphide, CuS, which is separated from solutions of $CuSO_4$ by H_2S, is very slightly soluble in water, and its complete separation depends on the following circumstances : The minimal quantities of CuS which dissolve and are dissociated into $Cu^{\cdot\cdot}$ and S'' are in a certain equilibrium with the precipitated and non-dissociated CuS: $Cu^{\cdot\cdot} + S'' \rightleftarrows CuS$; and according to the mass law (p. 68) we may always represent this equilibrium by a mathematical expression, taking the concentration of the ions (a for $Cu^{\cdot\cdot}$ and b for S'') and the concentration of the undissociated substance ($CuS = c$) into account; at a given temperature the general formula will be $a \,.\, b = k \,.\, c$, where k is the equilibrium constant (p. 102) which depends on the temperature only (the concentration of the saturated solution is different at different temperatures).

The product, $a \,.\, b$, which has a definite value for each saturated solution, is called the *solubility product* and indicates for any given temperature the concentration limit which must be exceeded in order that a precipitate may commence to be formed; $a \,.\, b$ is also the *concentration product*, that is, it represents the concentration of the ions at a definite temperature. The two products coincide in the case of saturated solutions, but sometimes the concentration product exceeds the solubility product. This is the case for supersaturated solutions in which, as soon as the labile equilibrium ceases, so much salt separates that the concentration product becomes equal to the solubility product. If in the case of a given salt the concentration product is inferior to the solubility product, we have an unsaturated solution. In the case of slightly soluble salts the solubility product is very small, whilst in the case of very soluble salts it is comparatively large. In the case of precipitates, these are not able to form and separate until the concentration product of their ions has reached the value of the solubility product. When we increase the number of $H^{\cdot}$ ions in a solution of copper sulphate through which H_2S is passing, by the addition of a strong mineral acid, the ionisation of the H_2S is lessened, and the concentration product of the S'' and $Cu^{\cdot\cdot}$ ions becomes less than the solubility product, that is to say, it does not reach the saturation limit and consequently no CuS precipitate is formed. If we now alter the concentration of the $H^{\cdot}$ ions by considerably diluting the solution with water, then as further H_2S passes in, its ionisation and the concentration of the S'' ions may reach and exceed the value of the solubility product and the CuS will be precipitated.

This precipitate is very insoluble, that is, its solubility product is very small, and if, therefore, CuS is suspended in water acidified with a strong mineral acid, very little CuS will pass into solution because very few $Cu^{\cdot\cdot}$ and S'' ions suffice to attain the value of their solubility product which is minimal, and then no further traces of CuS will pass into solution. If, on the other hand, we are dealing with a metallic sulphide which is more soluble than that of copper, such, for instance, as ferrous sulphide, or to a still greater extent zinc sulphide, the solubility product will always be higher than the concentration product because H_2S is always only slightly dissociated, and thus these sulphides dissolve in mineral acids and are not precipitated in presence of hydrogen sulphide. These sulphides, however, can be precipitated by employing precipitating agents which do not contain $H^{\cdot}$ ions, which would cause the solution of the sulphide, and of these ammonium sulphide is very suitable :

$$ZnSO_4 + (NH_4)_2S = SO_4(NH_4)_2 + ZnS.$$

In the case of metals which give sulphides still more soluble than zinc sulphide, it is not possible to precipitate them with H_2S or even with $(NH_4)_2S$. The sulphides of the alkali and alkaline earth metals come under this category.

COPPER ARSENATE. In addition to various natural copper arsenates [*tricalcite*, $Cu_3(AsO_4)_2,5H_2O$; *olivenite*, $Cu{\cdot}Cu(OH)AsO_4$; *tyrolite*, $Cu^{\cdot}(CuOH)_4(AsO_4)_2,7H_2O$, etc.,

etc.] and *copper arsenite* (or Scheele's or Swedish green, $CuHAsO_3$, prepared by treating 100 kilos of copper sulphate dissolved in 500 of water with 12 kilos of arsenious acid dissolved in a solution of 20 kilos of potassium carbonate and hydroxide), use is nowadays made of a certain quantity of *copper arsenate*, $Cu_3(AsO_4)_2, 4H_2O$, which is obtained as an amorphous, blue powder, by treating at 50° to 60° a solution of copper nitrate and calcium arsenate.

In 1914 Italy produced 8000 kilos of copper arsenate, valued at £960.

GENERAL REACTIONS OF COPPER COMPOUNDS

Copper salts, excepting the sulphides, when treated with ammonia first form a hydroxide, which then immediately dissolves in excess of ammonia, producing an intensely blue solution which on evaporation deposits crystals having a constitution similar to double or basic salts such as $CuSO_4, 4NH_3, H_2O$, this giving $CuSO_4, 2NH_3$ at 150°. These salts contain complex ions and therefore only show a few of the general reactions for copper. Thus they are precipitated by H_2S but not by KOH. Volatile copper compounds colour the flame blue or green. The blue ammoniacal solutions are decolorised by addition of potassium cyanide, as compounds are obtained which no longer contain the $Cu^{\cdot\cdot}$ ion. With potassium ferrocyanide (*see* Iron), cupric salts give a reddish-brown coloration or precipitate of copper ferrocyanide.

On immersing a bright strip of iron in a solution of a copper salt it immediately becomes covered by a layer of metallic copper.

SILVER: Ag, 107.88

Silver is a metal which has been known since remote antiquity, as it is often found free in nature.

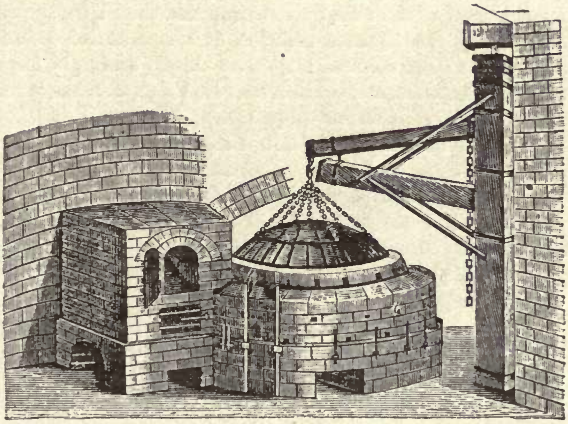


FIG. 275.

The principal minerals from which it is extracted are *Argentite*, Ag_2S, *Pyrargyrite*, $3Ag_2S,Sb_2S_3$, *Strohmeyerite*, Cu_2S,Ag_2S, and *Horn Silver*, AgCl.

It often accompanies lead in galena in quantities sufficiently large to enable it to be profitably extracted. Argentiferous galena ordinarily contains 0·01 to 0·05 per cent., and occasionally 1 per cent. of Ag, and constitutes the most important ore from which silver is extracted.

Silver ores abound in California, Mexico, Chili, Saxony, Hungary, the Altai Mountains, and a little in Sardinia.

The metallurgy of silver is fairly varied, and according to the local circumstances silver is extracted sometimes by one method and sometimes by another. In the past amalgamation processes were used, but solution processes are now gaining ground. We shall describe concisely the more important processes.

DRY PROCESSES : (1) *Extraction by Lead.* This is based on the property of lead and lead oxide of displacing silver from its compounds on heating. Whilst the other metals separate in the form of oxides, silver is not oxidised and remains dissolved in the molten lead. The argentiferous ore is mixed with lead (galena containing at least 0·15 per cent. of Ag is treated as such), and is melted in a cupel furnace (Fig. 275), which is a reverberatory furnace with a circular brickwork hearth lined with stamped calcareous marl and containing a depression in the centre in which the molten silver collects. The cupel, which may contain as much as 40 tons of lead, is closed by a sheet-iron cover capable of being raised and removed and is lined internally with clay. During smelting a current of air is injected by a mechanical blower and two tuyères which pass into the cupel; oxidation is continued until all the lead is transformed into the molten oxide (litharge). The cupel is heated by a furnace at the side, separate from the cupel itself, and in order to discharge the molten litharge which floats on the surface there are two lateral openings, the sills of which can be lowered so that all the PbO can be removed continuously whatever may be the level of the molten mass.

Finally molten silver alone remains, covered by a thin layer of PbO which bursts occasionally and reveals the shining surface of the molten silver and an iridescent light.

Part of the lead oxide, together with other impurities, is absorbed by the porous base of the cupel. When the iridescence is observed, the completion of the cupellation is assumed, and the cooling of the silver may be accelerated with water. This final product is still impure, containing 95 to 98 per cent. of silver, together with other metals, which are then separated by refining in another much smaller reverberatory furnace with a porous floor, by the help of a strong air-blast, which oxidises and separates all the other oxidisable metals in the form of slag, with the addition if necessary of a little marl or bone ash. When the metal is pure it is removed from the furnace, and may be either granulated by pouring it into water or poured into moulds in order to be cast into bars.

(2) Another dry process is that proposed by **Pattinson** in 1833, which is well adapted for the treatment of lead containing less than 0·01 per cent. of Ag. In the same way as, on freezing the aqueous solution of a substance, the solid solvent is almost exclusively separated in the form of ice, so on slowly cooling a large mass, even 10 tons or more, of molten argentiferous lead in a cast-iron pan, octahedral crystals of lead separate which are much less argentiferous (liquation). The solid portions are removed with perforated ladles, and the remaining liquid lead containing more silver is allowed to cool continuously, the solid lead being removed as fast as it forms. An argentiferous lead containing 1 to 2·5 per cent. of Ag finally remains, whilst the separated portion does not contain more than 0·001 to 0·003 per cent. The argentiferous lead which has thus been enriched is then subjected to cupellation as described above.

When argentiferous ores are treated by Pattinson's process it is necessary to mix them with much pure lead.

(3) A third dry process, for which pure lead is not required as in Pattinson's process, is that proposed by Karsten in 1841 and applied unsuccessfully by Parkers in 1850. After various improvements by Roswag, Cordurié, and others, the process was successfully introduced industrially. It is based on the fact that zinc has a greater affinity for silver than lead.

The argentiferous lead under treatment is melted in large cast-iron pans of a capacity of 2 tons or more and heated to a temperature of above 450°, that is, a little higher than the melting-point of zinc. About one-fifth of a ton of zinc is then added in several portions and the mass is kept mixed for a long time, the impurities which collect at the surface being separated.

The zinc combines with all the silver, a little lead, and any impurities such as copper and gold. A dense scum then collects at the surface and solidifies on slowly cooling, floating on the molten lead so that it is easy to separate it a little at a time. The remaining lead should not contain more than 0·001 per cent. of silver. The argentiferous zinc is then treated in one of two ways. It may be cupelled in the same way as argentiferous lead, or preferably it is distilled in a graphite crucible mixed with a little carbon (1 per cent.). The zinc which distils is condensed and re-utilised.

Schnabel, on the other hand, melts the zinc scum in a closed iron pan provided with a delivery tube for the gases, H, air, etc., and passes in a jet of steam at a pressure of 2 atmospheres. In this way zinc oxide and lead oxide are formed and separate. The hydrogen which is evolved mixes with air and produces slight explosions now and again. All the silver remains mixed with the lead, which is finally treated in the cupellation furnace.

WET PROCESSES. These comprise the European and American amalgamation processes and the solution process.

(1) **European Amalgamation Process.** This is based on the fact that mercury easily alloys with and dissolves silver, and reacts with certain silver compounds, such as Ag_2S and AgCl, forming amalgams. The powdered ore is mixed with sodium chloride and

gently roasted in a reverberatory furnace, in cupola furnaces or in a Brückner rotary furnace. Sulphates and oxides are formed and the silver is converted into chloride. After cooling, the powdered mass is placed in a revolving barrel with a little water and lumps of iron, and is kept in motion for some hours.

The silver chloride which was dissolved in the sodium chloride is decomposed by the iron : $2AgCl + Fe = FeCl_2 + 2Ag$.

The free silver is amalgamated by adding an excess of mercury in the same barrel and rotating it for 18 to 20 hours. The amalgam, containing all the silver, is filtered through sacks in order to separate the excess of mercury and the aqueous solution, which pass through the cloths. By applying a little pressure to the cloths, a little further mercury is pressed out, and the remaining amalgam is distilled in various ways in order to separate the mercury, which is easily volatile, from the less volatile silver.

The distillation is conducted in horizontal cylindrical iron retorts with a delivery tube which dips into a vessel of water where the mercury vapours are condensed. The remaining silver is then refined in any suitable manner.

(2) **American Amalgamation Process (Patio Process).** This process is especially used in Mexico. The ore is finely powdered, and is then placed in large flat heaps in yards with an inclined pavement, and is sprinkled with water and salt (2 to 5 per cent.). An intimate mixture is obtained by causing men and mules to trample on the heaps for some days and 2 to 3 per cent. of cupriferous chlorinated burnt pyrites or roasted chalcopyrite is then added. The mixing is continued, and finally the necessary quantity of mercury is added to each heap, namely, 6 to 8 kilos for each kilo of silver contained in the ore.

The whole is incessantly mixed for 40 to 50 days by making horses trample over it in such a way that complete amalgamation is secured. The chalcopyrite forms ferrous chloride with the sodium chloride and copper, and also sodium sulphate.

With the silver these chlorides form silver chloride, which remains dissolved in the excess of sodium chloride and forms calomel (HgCl) and free silver by interaction with the mercury. This silver then dissolves in the mercury, forming an amalgam. The amalgam is separated from many impurities with water in revolving barrels, and is then filtered through sacks, after which it is distilled as described above. This process is very lengthy and causes considerable loss of mercury (as HgCl) and of silver, but it has the advantage of not requiring fuel until the amalgam is formed, and it is possible to treat ores which cannot be utilised by other methods.

(3) **Kröhncke's Process.** This treatment takes place in revolving barrels with a hot solution of cuprous chloride and sodium chloride. Silver and AgCl are so obtained, even in presence of arsenic and antimony sulphides. Mercury is then added, together with zinc or lead, so that amalgamation may take place without loss of mercury in the form of HgCl. The process is rapid and rational, and is accompanied by a minimum of losses. The amalgam which is finally distilled ordinarily contains about 10 per cent. of silver.

(4) **Various Processes.** Francke's process is an improvement on the American process. The ore is partially roasted with NaCl, and the silver is thus obtained partly as chloride and partly as sulphate. The silver is then separated from solution by copper plates and is finally amalgamated. Another process consists in treating minerals containing native silver or much silver chloride or sulphide with a hot solution of NaCl in copper vats furnished with copper stirrers and heated over direct fire. Cuprous chloride is formed and decomposes the silver sulphide. The silver is then amalgamated with mercury.

(5) **Solution and Precipitation Processes.** (*a*) Augustin's process. This process is useful for pure sulphides or argentiferous copper matte, as far as possible free from Pb, Zn, Sb, and As.

The powdered ore is mixed with sodium chloride and roasted, and is then extracted with a solution of sodium chloride in revolving barrels; this dissolves the silver chloride, forming a double salt. The silver is first precipitated from the solution by copper plates and the copper then recovered by dissolving it and precipitating it with iron.

Gibbs modified this process by precipitating the last portions of silver mixed with cuprous chloride fractionally with sulphuric acid; all the silver is found in the portions which separate first.

An advantageous simplification of Augustin's process, especially for the treatment of argentiferous alloys and rich ores, is that introduced by Ziervogel, who roasts in the absence of sodium chloride in such a manner that silver sulphate is obtained mixed with copper sulphate and basic ferric sulphate. The silver and copper sulphates are dissolved by boiling water, the silver being precipitated with copper sheet, and copper sulphate thus obtained as a by-product. This process is not suitable when the mineral contains Sb or As, because silver arsenate and antimonate are then formed during roasting and are insoluble in water, being thus lost. Recently C. Goldschmidt has advantageously replaced the copper or iron plates used to separate the silver from the sulphate by cobalt plates; the silver is at once deposited partly in an amorphous and partly in a crystalline condition.

There are other wet processes which use **Sodium thiosulphate** (Patera) or **Calcium thiosulphate** (Kin), which very easily dissolve the silver chloride contained in ores which have been roasted with NaCl. A portion of the heterogeneous chlorides is, however, first removed by lixiviation with water. The solution of silver thiosulphate is precipitated with sodium or calcium sulphide and thus Na or Ca thiosulphate is regenerated, the silver being separated as sulphide. By this method, which has been improved by Russel, any gold which may be present in the ore is also separated. The silver sulphide is then treated in the usual way by the processes already described.

Crude copper matte or black argentiferous copper may also be lixiviated with dilute sulphuric acid; this dissolves all the copper, and the argentiferous residue is then treated with lead by the dry process.

Pure silver is obtained in the laboratory by dissolving commercial silver, which always contains a little copper, lead, etc., in nitric acid. Silver chloride is then precipitated with HCl. The chloride may be fused with soda, when silver remains: $2AgCl + Na_2CO_3 = 2NaCl + CO_2 + 2Ag$, or it may be boiled with dilute potassium hydroxide and glucose; the silver which is thus separated is melted in a crucible of quicklime by means of the oxy-hydrogen flame.

PROPERTIES. Silver conducts heat and electricity better than any other metal (Table, p. 514). It has a white lustrous colour and a specific gravity of 10·4 to 10·6; it melts at 962° and boils at 2070°. When evaporated in the oxy-hydrogen flame, it forms bluish vapours. It does not oxidise in the air when either hot or cold, and is therefore classed amongst the noble metals (Pt, Au, Ag). When molten it is able to absorb 20 times its volume of oxygen, which it loses suddenly on cooling (spitting). It crystallises in octahedra, and melts to a compact mass if it contains traces of Pb and Cu. It is not attacked by weak acids in the cold, with the exception of nitric acid, which dissolves it easily. Hydrochloric acid does not attack it appreciably, but H_2SO_4 dissolves it on heating. Silver soluble in water has been obtained in the form of a colloidal solution by the ordinary methods (p. 109), or more easily by adding a solution of $AgNO_3$ to a concentrated solution of sodium silicate containing formaldehyde. It forms a reddish-brown solution, though other colorations are obtained by other methods (*see* Gold). It is oxidised by ozone in the cold and is blackened by H_2S. Silver is a relatively soft metal, and for practical purposes it is, therefore, alloyed with other metals, especially with copper, which renders it harder. The fineness of silver alloys is given in thousandths, and that of coinage is $\frac{900}{1000}$ (in Italy), that is, it contains 900 grams of silver and 100 of copper for coinage of above the value of two lire. For coinage of lower value, the fineness is $\frac{835}{1000}$ (in Italy). Silver articles ordinarily have a fineness of 750. The addition of very small quantities of zinc or cadmium tends to the production of alloys free from blow-holes and irregularities. Alloys containing much copper—50 per cent.—can be rendered white by the addition of Al or Ni.

Much silver is used for silver-plating other metals or alloys, by using the object to be plated as a cathode and a silver plate as anode, the bath being formed of a solution of silver cyanide in an excess of potassium cyanide. The dissolved double salt, AgCN, CNK, is dissociated, forming $Ag(CN)_2'$ and $K^{\cdot}$. The $K^{\cdot}$ acts on the double cyanide and separates Ag; thus

$$Ag(CN)_2K + K = 2KCN + Ag.$$

A sensitive reaction for the identification of silver in its soluble salts, other than the ordinary one with hydrochloric acid or other chloride (which precipitates white, curdy silver chloride, soluble in ammonia, potassium cyanide or sodium thiosulphate, but insoluble in nitric acid), is that of Whitby (1910), allowing of the detection of 0·00004 gram of silver per litre : a little of the solution is heated with concentrated sugar solution for two minutes and a little normal caustic soda solution added. If the liquid remains colourless (observed in a tall cylinder) silver is not present, but if a yellow coloration appears the amount of silver present may be judged by means of a colorimeter, comparative tests being made with solutions of known silver content.[1]

STATISTICS AND PRICES. The world's production of silver was 2482 tons in 1880, 4180 in 1890, 5600 in 1900, 6032 in 1907, 7035 in 1911, and 6984 in 1913.[2]

The price of silver formerly showed continuous diminution : £9 per kilo in 1870, £6 13*s.* in 1890, £3 6*s.* in 1903, and later £2 4*s.*

Almost the whole of the Italian output comes from Pertusola (Spezia) : 43,000 kilos in 1898, 20,500 in 1907. For silver in bars, dust or scrap the Italian statistics are as follows (kilos):

	1910	1912	1913	1914	1915	1916	1917
Production .	14,237	14,363	13,094	15,254	15,361	15,131	—
Importation .	37,737	58,719	71,854	83,854	70,635	38,105	59,719
Exportation .	16,721	14,323	10,436	6,464	24,747	57	19

In 1913 the United States produced 2,077,527 kilos of silver, 487,000 kilos coming from Nevada, and the rest from Montana, Utah, Idaho, Colorado, Arizona, etc.

SILVER OXIDE : Ag_2O. This compound is obtained as a brownish-grey precipitate from a solution of silver nitrate when treated with sodium or potassium hydroxide. It is slightly soluble in water to which it imparts an alkaline reaction, which leads one to suppose that the hydroxide $Ag{\cdot}OH$ may be formed in the solution, and acts as a strong base. This hydroxide has, however, not yet been isolated.

At 250° the oxide dissociates into $Ag_2 + O$, and is reduced to metallic silver by hydrogen

---

[1] Armani and Barboni (1910) detect traces of silver in metallic alloys or in articles of silvered copper or bronze by treating a few scrapings of the metal in the cold with nitric-sulphuric mixture (1 part nitric acid of sp. gr. 1·41 and 9 parts of sulphuric acid of 66° Bé.), which dissolves the silver but not the copper. A few drops of the cold liquid are diluted in a test-tube with 2 to 3 c.c. of water, then neutralised with 20 per cent. caustic potash solution and treated with alkaline formaldehyde solution (2 vols. of 30 per cent. formaldehyde and 1 vol. of 20 per cent. caustic potash solution). In presence of silver (even 1 : 200,000) a more or less intense violet coloration appears.

[2] The output of silver in different countries was as follows (tons):

	1907	1910	1912	1914	1915	1916
Mexico	2040·5	2096	2566	857	1231	—
United States . . .	1830·5	1500	1940	2254	2332	2267
Canada	397	932	993	885	828	799
Australia and Polynesia .	545	464	—	111	133	—
Germany . . .	387	—	440	155	—	—
Bolivia and Chile . .	210	467	151	24	120	—
Peru	163		290	286	293	—
Spain	127·5	—	130	131	142	—
British India . . .	—	—	—	7·4	8·8	—
Dutch Indies . . .	—	—	14·4	14·5	—	—
Central America . .	—	—	54	86	91	—
Japan	89	136	140	150	158	—
Austria-Hungary . .	55	—	60	49	—	—
Greece	23·5	—	25	18	—	—
Turkey	16·3	—	30	46	—	—
Africa	16	—	35	33	—	—
France	7	—	45	16	—	—
Norway . . .	5·5	—	8·4	13	—	—
Russia	5·2	—	10	15	—	—
England . . .	4·3	—	15	4	—	—
Columbia . . .	—	—	26	11	—	—
Other countries . .	90	—	23	14	6	—
Whole world . .	6030	7000	7804	5202	5591	5517

In 1910 England imported silver ore to the value of £1,800,000.

France exported 23,524 kilos of silver in 1913 (imports 6100 kilos), 35,015 in 1914 (imports 9330 kilos), and 6298 in 1915 (imports 3385 kilos).

at 100°. The freshly precipitated oxide dissolves in ammonia, and its solution on evaporation leaves black crystals of $Ag_2O,2NH_3$, which when dry explode with a minimum amount of friction.

SILVER SUBOXIDE : Ag_4O, and SILVER PEROXIDE : Ag_2O_2. The first compound is very unstable and the second is obtained from silver or silver oxide in contact with ozone. It forms black crystals which yield oxygen and silver oxide at 100°.

SILVER CHLORIDE : AgCl. This compound is found ready formed in nature as *horn silver* and may be obtained as a white curdy mass by precipitating a soluble silver salt with HCl or with a soluble chloride such as NaCl. It blackens in the light. It is very slightly soluble in water (1 : 716,000 at 14°), but is easily soluble in ammonia, potassium cyanide and sodium thiosulphate solutions, forming various complex ions. It is insoluble in dilute acids, but dissolves in fuming HCl and in a concentrated solution of NaCl (*see* Processes of Silver Extraction).

It melts easily, forming horny masses on solidification. It is transformed by HI into AgI.

SILVER BROMIDE : AgBr. This is formed in an analogous manner to the chloride, and has a pale yellow colour. It is soluble in sodium thiosulphate and slightly soluble in ammonia. It forms AgI with HI. It blackens in the light more rapidly than the chloride.

SILVER IODIDE : AgI. This has a more marked yellow colour than the bromide, and is obtained under the same conditions as the chloride and bromide, but blackens more easily in the light when it contains traces of impurities, such as silver nitrate, tannin, etc. It is insoluble in ammonia and dissolves in HI, forming crystalline AgI,HI.

It is transformed by bromine or chlorine into AgBr or AgCl, as might be foreseen from its heat of formation.

SILVER FLUORIDE : AgF. This compound is readily soluble in water and has been proposed as an energetic antiseptic by Paterno and Cingolani, who placed it on the market under the name of *tachyol.* They proposed it for the sterilisation of water, but the favourable results obtained by them were contested by others (*see* Water, p. 236). Lo Monaco recommended its use for disinfecting mulberry leaves in order to prevent certain diseases of the silkworm. The results obtained were, however, not decisive. According to observations made by G. de Rossi, silver nitrate is as efficient an antiseptic as the fluoride. Paterno and Cingolani stated (1907) that whilst the nitrate sterilises water at a dilution of 1 : 200,000, the fluoride sterilises it more persistently even at a dilution of 1 : 400,000.

SILVER NITRATE : $AgNO_3$ (Lunar Caustic). This substance is easily obtained by dissolving commercial silver in dilute nitric acid and then evaporating. In order to eliminate the copper nitrate present as an impurity, the mass is melted and heated to a dull red heat in order to separate the copper in the form of oxide insoluble in water. It is obtained crystallised from an aqueous solution in rhombic tablets, isomorphous with KNO_3; it melts at 218°, and when solidified in the form of sticks forms *lunar caustic,* which is used in medicine as an energetic caustic for wounds and sores. It is very soluble in water and shows neutral reaction. It also dissolves in alcohol, and is poisonous. When pure it is not discoloured by light.

It is used in photography, in medicine, for silvering mirrors, etc. The price varies somewhat. The crystalline product costs £2 12*s.* to £2 16*s.* per kilo, and when fused in sticks £3 per kilo. Italy imported 6325 kilos in 1906, 3358 kilos in 1907, 2216 kilos in 1908, and 2990 kilos in 1909, of the value of £7200. A considerable portion of the imports came from Germany.

SILVER NITRITE : $AgNO_2$. This compound is formed by precipitating a concentrated solution of $AgNO_3$ with KNO_2. It crystallises from hot water in yellow needles.

SILVER SULPHITE : Ag_2SO_3. This is prepared as a gelatinous white precipitate by adding sulphurous acid to a solution of silver nitrate. It blackens in the air and decomposes at 100° with formation of silver.

SILVER SULPHATE : Ag_2SO_4, is obtained by dissolving spongy silver in hot H_2SO_4, and evaporating until crystallisation commences.

The colourless crystals dissolve in 200 parts of water and more easily in water acidified with HNO_3 or H_2SO_4.

SILVER AZIDE : AgN_3. Angeli prepared this substance from an aqueous solution of silver nitrate by the addition of an aqueous solution of hydrazine sulphate. It is not affected by light and is explosive.

THE PHOTOGRAPHIC PROCESS

It is generally known that the photographic process is based on the alteration of certain silver salts under the action of luminous rays, especially of the violet and ultra-violet rays. The first photographic processes were the *daguerreotype* process and the wet-plate collodion process, but these are now of historic interest only.[1] To-day dry-plates sensitised with gelatine containing silver bromide are exclusively used. They are prepared as follows in a dark chamber: A mixture of gelatine and silver nitrate is mixed with another mixture of gelatine and ammonium bromide at such concentrations that the gelatine sets on cooling.

The silver bromide thus produced is so finely divided that the solution becomes only opalescent and is not very sensitive to light, because it is still too transparent. In order to render it more sensitive, this solution is heated for a long time, so that the silver bromide

[1] **History of Photography.** The true photographic process commenced to acquire practical importance only after the beautiful experiments made by Daguerre in 1838, following which he succeeded in fixing the images of objects and persons in an easy, rapid, and permanent manner by the action of light. His success and the general admiration were so great that the French Government, on the advice of the celebrated Arago, offered Daguerre an annual pension of 6000 francs on condition that he made his discovery public. On August 19, 1839, at a memorable meeting of the Académie des Sciences, Arago communicated in detail the photographic process of Daguerre, and the daguerreotype process dates from that time. The substance sensitive to the action of light was silver iodide, which Daguerre produced on a silver plate by exposing it in the dark to the action of iodine vapour. In the camera this plate was rapidly affected by luminous rays emitted by the object to be photographed, although the image was not at once visible on the exposed plate. On exposing this plate to the action of mercury vapour, the mercury was deposited in extremely fine drops only on those parts which had been influenced by the light, and the image then appeared in full detail. All that was required in order to fix the image and render it stable in the light was to dissolve the unaltered silver iodide with a solution of sodium thiosulphate.

The essential difference between the daguerreotype process and those which had preceded it consisted in the fact that it was not necessary to expose the sensitive surface for a long time in order to produce the image, but by utilising the extraordinary sensitiveness of silver iodide it was produced in an extremely short time, so that it became possible for the first time to obtain a latent, invisible image even from moving objects, which could then be fully developed in all details by the above-mentioned indirect process.

By the daguerreotype process reproductions of the original photograph could not be obtained, but in the same year (1839) Talbot communicated to the Royal Society of London a method of obtaining several copies from one transparent original. He superposed the negative plate on paper sensitised with chloride and silver nitrate, and then on exposure to the sun he obtained the positive. In this manner he succeeded in obtaining any number of copies by repeating the same operation. On this principle, Talbot also obtained impressions directly in the camera on sheets of transparent paper coated with silver iodide, then developing the latent image with gallic acid, which precipitated black silver at the points influenced by the light. With this negative Talbot obtained the positive by superposing it on a sheet of sensitised paper and exposing to the sun. After developing the new exposed sheet with gallic acid a positive was obtained in the same manner as before, and any number could be obtained at pleasure.

A further important step in the development of photography occurred in 1847 when Niepce, a nephew of Daguerre's first assistant, obtained the first sensitive glass plate by fixing silver iodide on it with a layer of albumen, which, however, very easily altered. Fry and Archer obtained much better results in 1851 by coating the glass plate with a thin layer of collodion in which they had previously dissolved a bromide or an iodide. On immersing these plates in a bath of silver nitrate they obtained plates covered with an extremely sensitive film containing silver bromide or iodide, which after being exposed in the camera and developed with pyrogallic acid allowed extremely fine positives to be obtained which were faithful images of the object which had been photographed.

This convenient process with the collodion plate rapidly and completely replaced the daguerreotypes.

The collodion plate was supplanted in turn by a still more perfect process by which it was not necessary to prepare the plates a few minutes before use. In place of the wet collodion plate, Bennet succeeded, after the fruitless attempts of Maddox and Wortley, in preparing sensitive dry-plates coated with silver-bromide-gelatine, which could be kept for years.

aggregates into larger particles (Colloidal Solutions, p. 105), thus rendering the mass opaque (mature). According to W. Ostwald, the maturation of bromide gelatine plates is due to the fact that gelatine at first contains small and larger particles, and that, the former being more soluble than the latter in the solvent (gelatine solution), they dissolve first to form supersaturated solutions which allow the other particles to enlarge to maturation (*i. e.,* to maximal sensitiveness). This gelatine is then spread in thin layers on glass plates which are dried in the dark.

These are the ordinary photographic plates which are exposed in the photographic camera and receive light impressions from the illuminated object, the image of which is to be produced. Their sensitiveness is twenty times greater than that of the collodion plate, and Rayleigh has succeeded in producing a photographic impression on such plates with an exposure of a twenty-five-millionth of a second.

At the points which are exposed to the light, the silver bromide appears to be transformed instantaneously into silver subbromide, Ag_2Br (some say into silver), which is not visible, but forms a latent image which may then be rendered visible by treating it in a developing bath containing a reducing solution of ferrous potassium oxalate, eikonogen, hydroquinone, etc., in a chamber illuminated by red light, which has no action on the sensitised gelatine.[1]

In this way the Ag_2Br is reduced to black, finely divided, metallic silver which is deposited more or less abundantly on the plate, according to the intensity of the luminous impression.[2] It is maintained by some that the latent image is due not to chemical reactions, but only to physical modifications, because the latent image is obtained even at temperatures of — 252°, at which it is difficult to imagine any such chemical action.

---

[1] Ferrous oxalate dissolved in excess of potassium oxalate or a mixture of ferrous sulphate and potassium oxalate was first used as a developer, the bath being slightly acidified by preference. A more energetic alkaline developer, which had already been used for wet plates, was very soon used for dry plates, namely, an alkaline solution of pyrogallic acid treated with sodium sulphite. Later a slower developer was advantageously used for over-exposed plates, namely, hydroquinone and also its isomeride, pyrocatechol. For instantaneous negatives the best results are obtained with eikonogen, which is a very energetic developer consisting of the sodium salt of α-amino-β-naphtholsulphonic acid. It would be impossible to enumerate all the various developers which have been placed on the market during the last few years, such as metol, rhodinol, etc., which are suitable for even the finest work, but are only used, like those just mentioned, in a weakly alkaline bath.

Amidol, on the other hand, which is a sulphate of diaminophenol, develops the plate in a weakly acid bath in the same way as ferrous oxalate, and has less action on the gelatine film of the plate.

Only a few years ago photographic plates still had a great disadvantage, namely, that they were not uniformly influenced by the various colours of the objects which were photographed. The silver halides contained in the gelatine are very sensitive to blue and violet light, that is, to the more refractive rays of the spectrum, but are almost unaffected by green, yellow, or red light. It thus happens that a green or red flower or ribbon remains darker in the photograph than one of blue or violet colour. The credit for having indicated a way of obviating this difficulty as long ago as 1873 belongs to H. W. Vogel, who suggested the addition of substances capable of absorbing red, yellow, and green rays (*optical sensitisers*) to the silver-bromide-gelatine emulsion. At first mixtures of silver bromide with green or red aniline dyestuffs were made, but to-day silver salts are directly prepared from such colours, especially from eosin, etc. *Orthochromatic* plates are thus obtained which enable landscapes to be more faithfully depicted, and to-day still more perfect plates are produced by Miethe, called *perchromatic* or *panchromatic* plates with ethyl red (iodoethylquinaldine-quinoline) which are sensitive not only to the green and yellow rays, but also to an equal extent to all the rays of the spectrum including red. It has thus become possible to reproduce any painting with a sufficient truthfulness of shade, which was not possible in the past.

Among the improvements introduced into photography we may mention also the preparation of *films,* which are celluloid sheets covered with gelatine-silver-bromide emulsions like the glass plates. The films have the advantage that they can be produced in the form of rolls which take up little space and are also very much lighter than the glass plates.

[2] The more or less intense coloration obtained by the development of plates influenced by light is given by the particles of silver separating, these being larger or smaller according to the intensity of the luminous action. Lüppo-Cramer (1910) reproduced these various colorations artificially with larger and smaller particles of colloidal silver inoculated into a gelatine-silver nitrate solution. Thus, addition to 100 c.c. of the latter (away from the light) of varying amounts of a 0·05 per cent. solution of colloidal silver, followed by reduction with alcoholic hydroquinone solution yields: bluish-grey with no colloidal silver, sky-blue with 0·5 c.c. of the colloidal silver solution, bluish-violet with 2 c.c., ruby-red with 5 c.c., and yellowish-brown with 10 c.c. The colour varies, therefore, with the number of silver nuclei added, and hence with the magnitude of the colloidal particles.

Of the various theories of the development of photographic images, the most acceptable appears to be that based on the electrolytic (ionic) dissociation of the developer solution.

When the image is well developed the plate is immersed in a bath of sodium thiosulphate (*fixing bath*) which dissolves only the unaltered silver bromide (not acted upon by the light) and the image thus remains fixed on a plate of transparent glass, but with shading opposite to that of the actual object, that is, the luminous portions of the object appear the darkest as they have influenced the plate to the greatest extent. In this way the so-called *negative* is obtained. Fixation is carried out in a place illuminated by a yellow light.

In order to obtain *positive* copies from the negative, that is, copies which reproduce the object in its true relations of light and shade, the negative plate is placed over a sheet of sensitised paper prepared by an analogous method to the plate, but with a gelatine which is less sensitive to light. On exposing the plate to the light this allows more or less light to pass through its more or less darkened parts, and thus produces the complete positive on the paper in a few minutes with shading corresponding with that of the photographed object. This printed paper is then treated in a dilute bath of gold chloride in order to obtain more intense and pleasing tints. This operation is called *toning* of the positive, and is due to very fine blackish particles of gold which are deposited at those parts of the paper more or less influenced by the light, the partially reduced silver salt acting in turn as a reducing agent on the gold salt. After toning, the positive is treated in a bath of sodium thiosulphate in order to dissolve the silver salt which has not been influenced by the light, and the positive is then said to be *fixed.* In order that the prints may remain stable and unaltered in the air, it is necessary to complete the operation by abundant and prolonged washing with water, as otherwise traces of thiosulphate remain and these slowly decompose, depositing sulphur and forming silver sulphide which has a yellow and unsatisfactory appearance even in thin layers. This disadvantage is sometimes caused also by the decomposition of the albumen of the paper, which itself contains sulphur.

The **Platinotype Process** is free from such disadvantages and forms prints of black shade, harmonious and similar to wood-cuts, and is greatly valued. Platinotype paper is prepared with ferric oxalate and potassium chloroplatinate. The ferric oxalate is reduced to insoluble ferrous oxalate by the action of light, and this is then able to reduce the platinum salt on simple immersion in water or in a solution of potassium oxalate, thus separating very fine black particles of platinum, which form and intensify the shades of the printed copy. Simple washing in water acidified with hydrochloric acid then suffices in order to obtain, without any further fixing, a suitable print which is almost completely resistant to the action of chlorine.

It is thus clear in what manner as many copies as are desired may to-day be printed from a single negative.

The **Catatype Process.** Before closing this very short chemical account of the origin and development of photography, we must record an interesting discovery due to Ostwald and Gros jointly in 1903, based on purely theoretical considerations on *catalysts,* which has met with practical success. In chemistry various reactions are known which occur more or less slowly, for instance, the action between pure zinc and pure sulphuric acid, which produces a minimal or almost zero quantity of hydrogen. If, however, a drop of platinum chloride is added, the development of hydrogen becomes abundant and tumultuous. Again, hydrogen peroxide slowly decomposes, forming oxygen and water, but if a trace of manganese dioxide is added, oxygen is evolved very abundantly. These substances, such as platinum chloride, finely divided platinum, manganese dioxide, etc., which take no part in the reaction, but notably accelerate it by their presence, are called *catalysts* (*see* pp. 71, 323).

Ostwald and Gros applied a very simple catalytic process to the copying or printing of photographs on paper without the action of light, starting from another photograph. It is known that a solution of pyrogallic acid oxidises slowly in presence of potassium bromate, forming reddish-brown colorations. If, however, a trace of powdered platinum or silver is added, the coloration is produced rapidly. In the ordinary photographic positive the image is formed by a deposit of finely divided silver or platinum. If a sheet of paper prepared with pyrogallic acid and potassium bromate is brought into contact with this positive in the dark, then after some time a positive copy with reddish-brown tones will be obtained. It is clear that the original positive used in this way will rapidly lose its colour and become quite useless. This objection can, however, be avoided by modifying the process in the following manner, which also permits a positive to be obtained from a negative.

If an ethereal solution of hydrogen peroxide is poured on to the negative plate, the peroxide is decomposed at the points of contact with the silver deposited on the plate, and water alone remains, whilst at the more or less dark portions of the negative the hydrogen peroxide remains unaltered. If after evaporation of the ether a dry gelatinised paper is applied with slight pressure to the negative, the hydrogen peroxide brought on to this sheet remains unaltered, thus forming an invisible positive. If the sheet is then treated with a solution of manganese chloride or sulphate, a brown deposit of manganese dioxide is formed at those points where the hydrogen peroxide is present, so that all the shades of the photograph are faithfully reproduced. If, on the other hand, it is treated with an alkaline solution of a silver salt a black deposit of silver will be formed; other similar tints may be produced with other solutions.

This process of copying or photographic printing is known by the name of *catatypy*, and it is believed that it will soon acquire practical importance, especially for platinum negatives or positives which have a more marked catalytic power than those of silver. *Luminography* also may apparently be extended to the copying of drawings and illustrations.[1]

During the last few years, after fruitless or almost fruitless attempts by Ritter, Wollaston, Davy, Becquerel, Ducos, Cros, and many others, a practical method of *colour photography* has acquired certain importance, and has approached a practical solution. At first the most varied chemical processes were tried without much practical success, and it was only in 1891, when G. Lippmann, by making use of an interference process, succeeded in faithfully reproducing all the colours of the solar spectrum in a permanent manner, that this branch of photography disclosed new and enormous horizons. Lippmann solved the problem in a very simple manner by placing the film of silver bromide, finely subdivided in gelatine, in contact with a mercury surface in the dark chamber of a photographic camera, and then allowing the coloured object to act on the plate. The plate is developed in the usual manner, but the photograph shows by reflections all the colours of the depicted object.[2] In 1908 the firm

---

[1] F. J. Smith (1901) proposed to utilise phosphorescence to reproduce photographically portraits and drawings (*e. g.*, of a book) without moving the originals. Behind the original is placed a luminous card (luminophore) and on the front is placed the sensitive face of a slow photographic plate. The book is then left closed under gentle pressure for 20 to 60 minutes, according to the thickness of the paper, the plate being then developed as usual. The luminous card is prepared by smearing with gum dammar containing per 100 grams: 20 grams CaO, 20 grams SO_2, 6 grams S, 1 gram K_2SO_4, 1 gram Na_2SO_4, 2 grams Li_2CO_3, 2 grams of starch, 2 c.c. of alcoholic 0·5 per cent. crystalline bismuth nitrate solution, and 2 c.c. of aqueous 1 per cent. rubidium nitrate solution. To copy an illustration with printing on the back, the latter is covered with a sheet of black paper, the procedure then being as before.

[2] F. Grassi summarises this interesting process of *colour photography* in his "History of Physics in the Nineteenth Century," as follows: "Lippmann uses a small vessel filled with mercury, one wall being formed by the sensitised plate with the gelatine film inwards. The vessel is then placed in an ordinary dark slide in such a manner that the film is in the normal position. The rays proceeding from the object, which we will suppose, in order to simplify the reasoning, to consist entirely of the red rays of the solar spectrum, pass through the film and encounter the surface of the mercury which reflects them in the same direction as the incident light. Stationary waves are thus formed and the film may be imagined as divided into many layers parallel to the surface of the glass, bounded by the planes in which the action of the light is at a maximum, and where, consequently, the sensitive substance of the plate will be most largely changed. Between the one plane and the other there will be half-way a plane in which the reflected light destroys the incident light and in which the sensitive matter will not have been in the least changed, because it has not actually been exposed to light. On developing the plate in the ordinary manner and fixing it, the film is now formed of many very thin layers each of which will have precisely that thickness which, as in certain portions of a soap bubble, appears red.

"When a multi-coloured object is photographed each of these colours will appear at the corresponding point in the image when it is looked at by reflected light, as each colour is determined by the thickness of the thin layers which have been developed on the gelatine according of Lumière, of Lyons, simplified and improved colour photography with their *autochromatic plates*, which are coated with starch grains coloured red, green, and blue, so that the plate is only influenced by colours corresponding with those of the starch grains. The red grains allow only red light rays to pass, and retain all the others; the same applies to the green grains and the green rays. Contrary to what might be supposed, even the most delicate intermediate shades are faithfully reproduced. The Lippmann process required a long exposure, whilst with the autochromatic plate even instantaneous photographs may be taken, but they cannot be reproduced. They are very suitable for projecting coloured pictures (in a lantern).

R. Luther (1911) obtained sensitive plates for colour photography by sensitising separately three emulsions coloured with three different colouring matters: one, for instance, with erythrosin (red), which will be sensitive only to the green part of the spectrum and insensitive to the red and violet; a second coloured blue and sensitive to the red and orange, and the third yellow and sensitive to blue and violet. The three emulsions thus sensitised are centrifuged separately, the masses of silver halides thus obtained being mixed in convenient proportions and the mixture emulsified afresh with a solution of colourless gelatine and poured on to the plates, which are then allowed to dry. The differently coloured silver halide granules are thus homogeneously distributed.

Since 1906 *catachromic* experiments have been proposed and made by K. Schinzel in which the exposed plate takes an inverse picture, and on printing thus reproduces the original colours of the object photographed.

Photography has given rise to numerous new and flourishing industries which have acquired enormous importance in certain countries. It will suffice to note that already in 1885 the United States consumed 40 tons of silver and 3 tons of gold for photographic preparations alone. In 1901 Germany exported for photographic purposes silver salts to the value of more than £48,000, and gold preparations to the value of more than £120,000. If we include in the photographic industries optical apparatus as well as chemicals, it is estimated that in 1904 the world's production exceeded £20,000,000, and that this industry occupied tens of thousands of workpeople. These figures have been almost decupled by the extraordinary development of modern cinematography.

GOLD: Au, 197.2

Gold is often accompanied in nature by silver (from 1 to 40 per cent.) and occasionally by mercury. It is generally found in the free state in quartzose or alluvial rocks and in the sand carried down by certain rivers. Thus we have the gold-bearing sands of Tessin and of the Adda. Gold is widely diffused throughout the earth's crust, but in such small quantities that it pays to extract it only in regions where it is relatively abundant, such as the United States, California, Alaska, Hungary, Transylvania, Russia (Ural), and the Transvaal. In Italy the production is minimal and the gold is found in grains imperceptible to the naked eye, contained as small veins in quartz and in auriferous pyrites at Monte Rosa in the province of Novara, and is extracted by an English company in the Val Sesia, Val Ansaca, and Val Toppa. A little gold is also found in the Val d'Aosta; at Bovisa, near Milan, the firm of Vogel extracts gold from roasted auriferous pyrites. Gold is rarely found in compact masses —nuggets—although in Australia a nugget weighing 87 kilos has been found. The ore treated in the Transvaal contains 20 grams of gold per ton, and is considered to be a rich ore.

---

to the characteristic wave-lengths of that particular colour. The method requires special precautions on account of the varying velocities characteristic for the different colours.

"We may note finally that these colour photographs are permanent, because the coloration does not depend on chemical circumstances which may become modified by light, but on the properties of thin plates, which properties are permanent because they depend on the thickness alone. It is thus evident that Lippmann photographs cannot undergo alteration."

Gold was formerly extracted entirely by levigation of sand and disintegrated auriferous rocks; the water carries away the sand, which is lighter, leaving the heavier grains of gold behind, but in this way much gold was lost, much labour was required, and the resulting product was impure. A great advantage was gained when the disintegration of auriferous quartz rock by means of powerful jets of water at a pressure of 4 to 5 atmospheres was thought of (Fig. 276); the rivulet thus formed is subjected to levigation by passing it along inclined channels in which the heavier particles of gold are deposited, whilst those of the gangue are carried away by the water. In order to avoid losses, a little mercury is placed in these inclined channels in order to dissolve and retain the gold. The amalgam is then treated in the manner described below. When mercury is not used, the impure gold residues are passed over a magnet in order to remove any iron, and are then fused with borax, soda, and nitre in order to separate impurities in the form of slag.

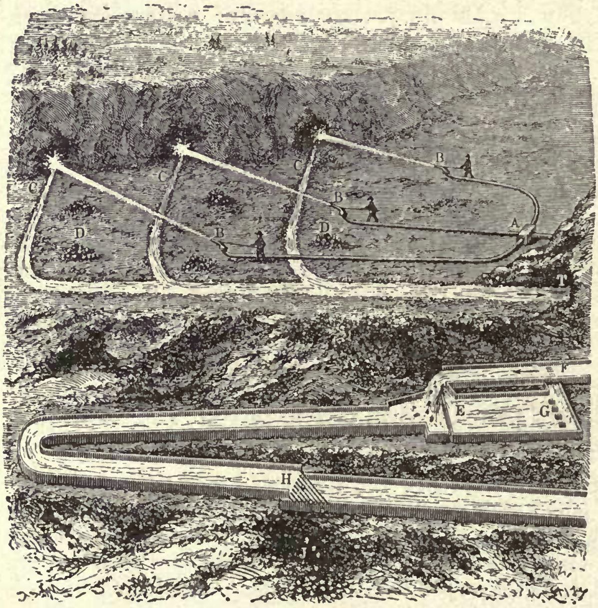


Fig. 276.

When gold-bearing deposits do not contain sulphides (pyrites, etc.), or after these have been decomposed by roasting, good results are obtained by extracting the gold by amalgamation. In this case the ore is very completely crushed and is carried by a stream of water into a rotating vat in continuous contact with mercury, which dissolves a large portion of the gold. In order to recover the small quantities of gold which are carried away with the mineral pulp together with the water, it is passed over amalgamated or silvered copper plates, to which an oscillatory movement is imparted. Now and again these plates are removed and the amalgam is distilled in the usual manner in iron retorts in suitable furnaces, when the mercury evaporates and the gold remains. In order to avoid minimal losses, the almost exhausted pulp is afterwards treated by the cyanide process described below.

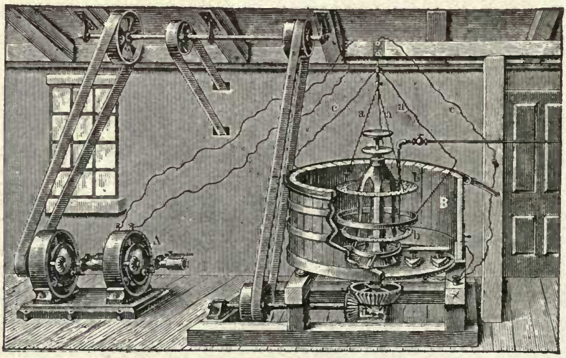


Fig. 277.

In order to amalgamate the gold in ores containing pyrites and arsenic, Rae has introduced with advantage electric amalgamation (Fig. 277), which is carried out in a wooden vat into which the auriferous pulp is passed with a current of water. An internal stirrer provided with perforated discs, b, forms an anode and is connected to the dynamo, A, by the leads a; the cathode is formed of mercury on the floor of the bath, and is connected with the dynamo through the leads c. By this process much labour and mercury are saved.

Amalgamation is not suitable for ores of complex composition, and these are treated by fusion with lead, which dissolves the gold, the impurities being then eliminated by fluxes in the form of slag. The auriferous lead is then treated by cupellation (*see above* under Silver).

A very advantageous process, by means of which up to 95 per cent. of the gold contained in ores is extracted, is that of Plattner, which consists in the chlorination of the ore. The latter is first roasted in order to eliminate the sulphur and arsenic, and is then moistened with water in a wooden vessel with a double bottom lined with paraffin wax or tar, in which it is then exposed to the action of chlorine. All the gold is transformed into gold chloride, which is soluble in water, and the solution is treated with ferrous sulphate in order to separate the gold in the form of a brown powder, which is then washed, dried, and fused with borax in order to obtain pure gold.

During recent years the process of A. Forrest, modified by Siemens, has come into general use. It is the most efficient of all processes and enables gold to be extracted even from very poor ores, and in general it can be employed without previous roasting. This process is based on the solubility of gold and of gold sulphide in sodium or potassium cyanide. The finely divided ore is generally first passed over oscillating amalgamated plates, and the pulp carried away by the washing water is then collected in large tanks of wood or masonry with a double bottom, which hold the product of the whole day's working—sometimes holding 800 cu. metres. To every ton of ore, half a ton of an aqueous 0·6 to 0·8 per cent. solution of potassium cyanide is added. The solution is changed every 24 to 48 hours, being replaced by a weaker solution, and the complete extraction lasts from 4 to 6 days, so that four to six vats are employed in order to permit of continuous working.

The reaction is given by the following equation, the oxygen being furnished by the air which is present in the ore and in the water :

$$Au_2 + 4KCN + H_2O + O = 2KOH + 2KAu(CN)_2.$$

In order to separate the gold from the solution of gold potassium cyanide Forrest precipitates it by introducing zinc or aluminium plates. W. Siemens, on the other hand, devised a considerable improvement by submitting the cyanide solution to electrolysis in vessels divided into several chambers in which anodes formed of iron plates or of lead peroxide are placed; the cathodes consist of thin sheets of lead on which the gold is deposited. At the anode Prussian blue is formed from which KCN is again obtained. Every month the leaden sheets, which now contain 1 to 10 per cent. of gold, are removed, and the gold obtained by cupellation, whilst the lead oxide formed is again reduced to lead. The residues from the electrolytic baths still contain 1 to 1·5 gram of gold per 1000 litres, whilst in the zinc precipitation baths only 0·2 gram remains. By means of the cyanide process, even 98 per cent. of the gold contained in the tailings and residues from the amalgamation process are to-day recovered, though they sometimes contain only 0·0002 per cent. of gold. These residues are separated by a process of decantation or are extracted two or three times in a filter-press with very dilute cyanide solution containing 0·02 per cent. of KCN.

The treatment of gold ores is now facilitated by powdering them more finely than was previously the case, and then using a filter-press and cyanide baths which circulate continuously; in this way the treatment costs less than £1 4*s.* per ton of ore.[1]

One of these electrolytic plants, 7 metres long, 1½ metres wide, and 1 metre high, consumes about 100 amps. at 2 volts and treats 50 cu. metres of solution per twenty-four hours. Since 1900 great economies have been effected in the cost of cyanide by employing

---

[1] A concentrated ore containing 40 per cent. Fe, 11 per cent. SiO_2, 1 per cent. S, and about 100 grams of gold and 25 grams of silver per ton, ground and levigated so that 98 per cent. of it passes through the 200 mesh sieve, gives only 75 per cent. of its gold on simple amalgamation, while treatment of the residue with cyanide brings the extraction up to 96 per cent. The same quantity of gold may also be extracted by merely treating a ton of the product with 1200 kilos of solution containing about 700 grams of sodium cyanide and about 1000 grams of CaO (the alkalinity of the lime accelerates the extraction and saves 25 per cent. of the cyanide) in a tubular ball mill, levigating and extracting the decanted residue with a somewhat more concentrated solution (about 900 grams of the cyanide and 1200 grams CaO). The first extraction lasts about 8 hours and the second (on the residue) about 4 hours, a current of air being used to stir in both cases. The residues are washed in special filter-presses with dilute cyanide solutions, and the gold precipitated from these by means of 200 grams of zinc dust per ton of filtrate.

the crude cyanide prepared by the Cyanid-Gesellschaft of Berlin from calcium carbide, atmospheric nitrogen, and potash (*see* p. 368).

Since 1910 the Clancy electrochemical process has been in use, this allowing of the utilisation of minerals which do not readily yield all their gold to mercury and which, with the cyanide process, require preliminary treatment, *e. g.*, roasting. Clancy easily obtains dissolution of all the gold from the finely powdered mineral by preparing an electrolytic bath with 907 kilos of ore and 907 kilos of solution containing 454 grams of sodium cyanide, 907 grams of calcium cyanamide (dissolved in water and filtered), and 227 grams of potassium iodide. The electrolysis is carried out in a vat with continual stirring and the conductivity is raised by adding sodium chloride (about 9 kilos); if an iron vat is used, this acts directly as cathode. With ferric oxide electrodes 90 cm. long and 7·5 cm. in diameter, each of these suffices for the treatment of 3600 kilos of ore.

The electrolysis lasts 8 hours, and at the end the solution is regenerated by adding 454 grams of caustic soda (to maintain the desired alkalinity), and about 25 grams of sodium cyanide, the current being passed for 2 hours to regenerate the cyanide in presence of halides and thiocyanates, which require marked alkalinity even during the electrolysis of the ore, so that the following reaction, $2ICN + Ca(CN)_2 = Ca(CN)_2I_2(CN)_2$, which allows of the complete exhaustion of the ore, may take place. In presence of sulphides, these are separated as thiocyanates (900 grams per ton of electrolytic bath). The costs per ton of ore treated are about 1·5*d.* for chemical reagents and 6·5*d.* for electrical energy (at 0·5*d.* per kilowatt-hour). The regenerated solutions should be filtered.

GOLD REFINING. When gold is admixed with silver and a little copper it is refined by heating it with nitric acid, which dissolves all the copper and silver if the silver is present in amount more than double that of the gold; otherwise it is necessary to add some silver.

A better method of refining, accompanied by less loss of silver, is carried out by heating with strong sulphuric acid, in which the gold only is insoluble. To-day the electrolytic process of refining by Möbius' process has become common, because it is very economical and yields very pure gold without noticeable losses of silver. The electrolytic bath consists of nitric acid or preferably of a feebly acid solution of silver nitrate. The mass of gold and silver under treatment is used as anode and is surrounded by cotton sacks; the cathode is formed of silver plates. All the metals of the anode, excepting the gold, which collects in the sacks, pass into solution, and at the cathode all the silver is recovered in a crystalline form.

If an electric current of 350 amps. per sq. metre at 1 volt is used, the silver has a purity of $\frac{999\cdot5}{1000}$, and the gold after fusion contains $\frac{999}{1000}$.

Use has been made for some years of the new electrolytic refining process of Wohlwill (U.S. Pat. 961,924, 1910) which permits of the use of gold alloys containing more than 6 per cent. of silver by means of an asymmetric alternating current obtained by joining in series a continuous current and an alternating current motor. As cathode thin gold leaves are used, and to the electrolyte, heated to 60° to 70°, gold chloride is gradually added in proportion to the gold separated; if lead is present, as much sulphuric acid is added as there is free HCl present (about 7 per cent. HCl).

PROPERTIES. Pure gold is a metal of a lustrous yellow colour, somewhat soft and extraordinarily ductile and malleable (p. 511); when in very thin sheets it shows a bluish or greenish colour by transmitted light. Its specific gravity at 17·5° is 19·33; it is an excellent conductor of electricity and heat and melts at 1054°, forming a green liquid. It is the most resistant of the noble metals, because it is attacked and dissolved only by aqua regia (a little by boiling nitric acid of sp. gr. 1·42), by chlorine and by potassium cyanide in presence of oxygen (*see above*). Mercury dissolves it without alteration, whilst it does not dissolve platinum, so that it is easily separated by this means. It is not oxidised in the air and always preserves its lustre.

Gold forms two sorts of compounds: *aurous* compounds, in which gold behaves as a monovalent element, and *auric* compounds, in which it is trivalent; the former are less stable than the latter and are decomposed, leaving gold, when heated.

Gold has been produced in colloidal aqueous solution (p. 109) of red colour by reducing a dilute solution of a gold salt with formaldehyde, preferably in the presence of sodium silicate. Blue colloidal gold solution is obtained by reducing a dilute and perfectly neutral solution (1 : 10,000) of $AuCl_3$ with a dilute solution (1 : 2000) of hydrazine hydrate.

In dilute solutions of gold salts, carbon monoxide produces a purple coloration due to colloidal gold, and this solution is very sensitive towards electrolytes. Alcoholic solutions of gold chloride, when poured into water, form hydrosols of various colours.

APPLICATIONS. As gold is very soft, it is only employed in the form of leaf for gilding works of art, fabrics, etc. For use in jewellery and coinage gold is always alloyed with copper, and then acquires a redder colour, or if it is alloyed with silver it acquires a lighter yellow colour. The fineness of gold in jewellery is expressed in carats. The pure metal is called 24-carat gold, and thus 18-carat gold contains 18 parts of gold in 24 (= 75 per cent.).

Gold coinage (Italian) has a fineness of $\frac{900}{1000}$ (English, Russian, and Turkish coins contain $\frac{916.5}{1000}$ of gold). Jewellers produce a pure gold colour on the surface of 18-carat gold by dissolving a large part of the copper from the surface by immersion in a bath of potassium nitrate, alum, and salt, or in HNO_3 or H_2SO_4. Gold is soldered with an alloy of silver, gold, and copper. In order to recognise gold objects and determine their quality approximately, the object under examination is rubbed on a *touchstone* and compared with another streak made with gold of known strength, by moistening both streaks with HNO_3; the effects obtained are then compared, and according as the streak of the object under examination disappears to a greater or less extent the purity of the gold is estimated. Objects are gilded by means of gold amalgam or gold leaf, or electrolytically in the same way as silver.

STATISTICS AND PRICES. The world's output of gold was 155,000 kilos in 1895, 389,500 in 1900, and 571,400 in 1905, and was valued at £91,520,000 in 1909; in 1914 it was 660,667 kilos and in 1915 707,897 kilos.[1]

---

[1] Gold produced in various countries (kilos):

	1912	1914	1915	1916
United States	138,000	139,731	157,158	139,600
Canada	18,900	23,262	28,494	29,000
Mexico	34,092	7,205	9,870	18,800
Central America	5,442	3,601	4,469	—
Brazil	3,184	4,060	3,648	—
Ecuador	400	451	821	—
British Guiana	1,324	1,695	1,574	—
Dutch ,,	434	757	676	—
French ,,	4,500	2,949	2,949	—
Peru	741	1,538	1,670	—
Venezuela	550	922	922	—
Austria	200	302	302	—
France	3,000	2,182	2,107	—
Hungary	3,200	2,633	—	—
Russia	43,562	43,014	43,936	47,000
England	1	30	29	—
Congo	940	1,354	2,713	—
Madagascar	3,000	1,655	1,314	1,250
Rhodesia	20,000	26,578	29,422	29,000
Transvaal	284,000	260,595	282,854	280,400
West Coast of Africa	10,638	13,049	13,256	12,000
British Borneo	2,500	1,940	1,977	1,800
,, India	—	17,120	17,328	17,000
China	5,000	5,454	5,529	5,400
Dutch Indies	5,000	7,057	4,906	—
Formosa	1,650	1,434	1,720	—
Japan	4,976	6,736	8,104	16,600
Corea	7,586	4,980	5,627	—
Southern Asia	713,867	75,106	73,903	62,000

In the United States the output of gold was about £20,000,000 in 1909, and £18,320,000 in 1912. The imports (from Mexico and Canada) were £12,200,000 in 1912, and the exports fell to £9,600,000 in 1912. The bulk of the production is from the Homestake mines.

France in 1913 exported 394 kilos of gold, in 1914 316 kilos, and in 1915 780 kilos, and imported 4520 kilos in 1913, 12,454 in 1914, and 1658 in 1915.

The price of gold was, in normal times, £137 10*s.* per kilo, and it varied only very slightly during the century preceding the European War (maximum variation 8*s.* per kilo), since it served to fix the value of all other wares and coinage.

AUROUS COMPOUNDS

AUROUS OXIDE : Au_2O. This is formed as a dark violet powder when potassium hydroxide is added to aurous chloride, AuCl. It decomposes at 250° into $Au_2 + O$.

AUROUS CHLORIDE : AuCl. This compound is formed by heating auric chloride, $AuCl_3$, to 180°. It forms a white powder insoluble in water, by which it is decomposed on heating: $3AuCl + 2Au$. It dissolves in ammonia, and from this solution HCl precipitates a white compound, $AuCl,NH_3$, which decomposes on drying.

AUROUS IODIDE : AuI. This separates as a yellow powder on treating a solution of auric chloride with potassium iodide, in an analogous manner to cuprous iodide: $AuCl_3 + 3KI = 3KCl + AuI + I_2$. On heating, AuI decomposes into its components.

POTASSIUM AUROCYANIDE: KCy,AuCy. This compound is formed on dissolving gold in excess of KCN in presence of oxygen, and is thus formed in the industrial extraction of gold. It is readily soluble in water, and is used for electro-gilding.

AUROUS SULPHIDE : Au_2S. This is separated as a grey powder, soluble in pure water, by passing H_2S into a hot solution of gold trichloride. It is reprecipitated from aqueous solution by HCl. It is used in gilding.

AURIC COMPOUNDS

AURIC OXIDE : Au_2O_3. This is obtained on heating a solution of auric chloride with magnesium oxide; the precipitate contains magnesium and consists of magnesium aurate, $Mg(AuO_2)_2$, and is treated with strong HNO_3; a brown powder of Au_2O_3 then remains, which, after drying, is decomposed at 250° into $2Au + 3O$. It is insoluble in water and acids, but is dissolved by alkalis as it has an acid character.

AURIC ACID : $Au(OH)_3$. If the precipitate obtained as above with magnesia is treated with *dilute* nitric acid, a reddish-yellow powder of $Au(OH)_3$ remains. This product does not show any basic reactions, but behaves as an acid and not as a hydroxide. It is insoluble in water and in acids and dissolves in alkalis on account of its acid character, forming salts of a hypothetical **Meta-auric Acid, AuO·OH**, which may be considered to be derived from auric acid by the separation of one molecule of water. **Potassium aurate** forms yellow needle-shaped crystals, $AuO{\cdot}OK + 3H_2O$. It is soluble in water, and has an alkaline reaction. It is formed from the oxide and KOH; on treating it with other soluble salts it forms other aurates. Thus, with silver nitrate it forms silver aurate:

$$AuO{\cdot}OK + NO_3Ag = NO_3K + AuO{\cdot}OAg.$$

Salts of normal auric acid are not known.

AURIC CHLORIDE : $AuCl_3$ (Gold trichloride). When chlorine or aqua regia acts on metallic gold a brown-red deliquescent mass is formed which is soluble in water, alcohol

---

The Italian Statistics are as follows (kilos):

	1910	1912	1913	1914	1915	1916
Imports	6105	4998	6564	3673	851	85
Exports . .	9056	9387	8943	4961	803	486
Production .	24	33	27	—	2	—

and ether, and consists of $AuCl_3$. On evaporating the aqueous solution it is partially decomposed into Cl_2 and AuCl. It is soluble in HCl, and on concentrating this solution by heating, long yellow needles separate, which consist of chlorauric acid, $HAuCl_4 + 4H_2O$, of which various well-crystallised salts are known, such as potassium chloraurate, $KAuCl_4 + 2H_2O$, and the ammonium salt, $NH_4AuCl_4 + H_2O$, which may also be considered as double salts, $AuCl_3,NH_4Cl,H_2O$ and $AuCl_3,KCl + 2H_2O$. Sometimes in solution these salts do not form an anion $AuCl_4'$, but behave like gold chloride.

GOLD SULPHIDES : Au_2S_3 and Au_2S_2. On passing a current of H_2S into a *cold* solution of auric chloride, a blackish-brown mass separates which is formed of a mixture of these two sulphides, together with a little sulphur. It is soluble in alkali sulphides, and then forms sulpho-salts (K_3AuS_2, etc.).

Solutions of *gold salts* in general are easily reduced to finely divided metallic gold by ferrous sulphate, oxalic acid, stannous chloride, etc. With the last reagent, a precipitate of purple-violet colour is obtained which is known as *Purple of Cassius*, and is probably nothing but a colloidal complex of finely divided gold and stannic acid, and is used for colouring glass and porcelain. This characteristic reaction of gold salts is not always easily produced, and it is necessary to add the stannous chloride slowly drop by drop to an excess of the gold solution.

THIRD GROUP. TRIVALENT METALS

These form the group of the so-called earths or earth metals, a name derived from the properties and appearance of the corresponding oxides, of which aluminium oxide (alumina) is the type. The group is formed of elements with a trivalent cation and includes **Aluminium** ($Al = 27{\cdot}1$), and a special group of very rare elements: **Scandium**, $Sc = 44{\cdot}1$; **Yttrium**, $Y = 89$; **Lanthanum**, $La = 139$; **Ytterbium**, $Yb = 172$; **Gallium**, $Ga = 69{\cdot}9$; **Indium**, $In = 114{\cdot}8$; **Thallium**, $Tl = 204$.

Aluminium has certain resemblances to boron in its valency and in the constitution of many of its derivatives. Thus both the elements are insoluble in nitric acid and soluble in boiling solutions of alkali hydroxides. Further, boron hydroxide has decidedly acid characteristics and aluminium hydroxide is also acid with respect to strong bases, with which both form salts of the same constitution: $B(ONa)_3$; $Al(ONa)_3$; still, aluminium, on account of its higher atomic weight, also possesses basic and metallic characteristics much more pronounced than those of boron. In general the elements of the sub-group have less basic characters in spite of their high atomic weights.

ALUMINIUM: Al, 27·1

This is an important element, not only on account of the applications which it has found as metal during recent years, but also because it is abundantly and widely present in nature in a state of combination, and its derivatives form products of great practical importance. It is not found free in nature, but is abundant in the form of oxide, Al_2O_3, which when pure and crystalline forms *corundum*. When coloured red or blue by small quantities of metallic oxides, it forms *ruby* or *sapphire*. When subdivided into very small rather hard crystals it forms *emery*. It also abounds in the form of hydrates of varied composition and then forms *diaspore*, Al_2O_3,H_2O, in rhombic crystals; *bauxite*, $Al_2O_3,2H_2O$, and *hydrargillite*, $Al_2O_3,3H_2O$. In the form of silicate it enters as a most important element into the composition of many rocks, and then, when it forms pure white deposits, takes the name of *kaolin*, which is the prime material for the manufacture of porcelain. In large impure deposits it forms *common clay*, and when combined with various other silicates forms *felspar*, $(SiO_3)_2Al,KSiO_3$, etc. Aluminium is also abundant in the form of *cryolite*, which is a double fluoride of sodium and aluminium, $3NaF, AlF_3$ (*see* Soda, p. 599), and is supplied by Greenland to the whole world, more especially for the manufacture of enamels (*see below*), and partly for the manufacture of aluminium and of opaque white glass. Aluminium also enters into the composition of *mica*, a double silicate composed of basic aluminium metasilicate and potassium or sodium metasilicate.[1]

It was first prepared by Wöhler in 1827 in the free state as a grey powder by heating a mixture of aluminium chloride and metallic potassium to redness, but is more easily obtained in small spheres by passing the vapours of aluminium chloride over red-hot potassium.

Aluminium was first prepared electrolytically by Bunsen in 1854 by decomposing the double chloride of aluminium and sodium, after others had attempted to decompose aluminium chloride alone without success. The difficulty was caused by the high melting-point of the chloride, and Bunsen lowered this considerably by mixture with NaCl, as Dumas had already done in 1832 in the preparation of potassium, and Wöhler in the preparation of magnesium. In 1854 St. Claire Deville made various attempts to prepare aluminium industrially by employing sodium instead of potassium, together with the vapours of aluminium chloride. He also improved the process of preparing sodium, and thus lowered its price, and consequently the price of aluminium dropped from £48 per kilo in 1855 to £15 in 1856, and in that year Deville succeeded in preparing 30 kilos.

The attempts made by various chemists to obtain aluminium electrolytically, especially from cryolite, $3NaF,AlF_3$, remained without practical results until 1886, when Deville prepared aluminium by a more or less improved process.

In 1883 the first patents of Grätzels on the electrolysis of cryolite were taken out, and in 1884 the brothers Cowles attempted to prepare aluminium from alumina and carbon by heating the mixture with an electric current, but obtained a product of little value. In 1887 the important French patent of P. Héroult appeared, by which it was possible to obtain aluminium at a very low price by the direct electrolysis of fused alumina. The enormous aluminium works at Neuhausen on the Falls of the Rhine were then erected in 1888, and this company immediately united with the Allgemeine Elektricitätsgesellschaft of Berlin, which obtained aluminium by the same method at a low price, according to a patent by Kiliani. In America the manufacture of aluminium in large quantities was started in 1890 by the process of Hall, who electrolysed fused alumina dissolved in a fluoride. When these patents were first applied grave difficulties were encountered in the preparation of pure aluminium, and various alloys of aluminium with copper were alone prepared. Pure aluminium was produced only after 1890. To-day aluminium is produced entirely by these two processes, which are constantly being improved.

The technical details of these processes are jealously kept secret by the manufacturers. The great difficulties consisted in finding vessels which would resist external heating to the extremely high temperature of molten aluminium, and were overcome by melting the alumina by means of an electric arc by immersing the electrodes directly in the mass. The electric furnace for the manufacture of aluminium is illustrated diagrammatically in elevation and plan in Fig. 278. The hearth, *K*, of the furnace is formed of suitably arranged compact graphite bricks, *A*, and is held firmly together by an iron box, *a*, through which are passed the copper terminals, *a′*, united to the negative pole of the source of current.

---

[1] Mica abounds in the older rocks and occurs in granite. It is often mixed, in small, shining, golden scales, with cave and river sand, and the golden colour, due to iron, has often given rise to the belief that scales of gold were present. In India, the United States, Ceylon, Canada, etc., there are important quarries of mica in large sheets, which can be split into very thin leaves as transparent as glass and as flexible as paper. These are used for making non-brittle, heat-resistant articles, *e. g.*, window-panes (for explosive factories), lamp-chimneys, stove doors, fittings for electrical apparatus, safety glasses for workers in chemical industries, welders, firemen, etc. It conducts heat and electricity poorly, and its hardness is 2 to 3 (Mohs' scale) and its density 2·8 to 3·1; it is not attacked by acids and may be fused in the blowpipe flame. The United States produced 441 tons of sheet mica and 2193 tons of scrap in 1908; in 1907 Canada exported 786 tons and India 1984. The exports from India in 1911 amounted to £200,000. The price of mica varies with the dimensions of the sheets from 1*s*. 7*d*. to 12*s*. per kilo.

The anode, *B*, consists of a bundle of carbon plates, *b′*, held together by an armature, *g* and *h*, the interspace between these plates being filled with a well-conducting material, such as copper or green wood. This anode is connected with the positive pole through the ring, *h*. The anode is suspended at *e* by a chain in order that it may be immersed more or less deeply in the molten electrolytic bath at about 800° to 900°. The furnace is covered by a graphite plate, *k*, which allows the anode to move in a vertical direction only in the opening, *i*. The furnace is charged and the gases (CO) escape through the openings, *m* and *n*. Nowadays short anodes of large section are preferred, *e. g.*, 40 cm. high and 35 × 35 cm. section; the consumption is thus diminished. The current density is usually 0·8 to 1 amp. per sq. cm. The electrolytic bath occupies less than 1·5 metre in length, 1 metre in width, and 50 cm. in height for a current of 8000 amps. The current yield is about 65 per cent. of the theoretical, 1 kilo of aluminium requiring 22 to 30 kilowatt-hours.

In the preparation of aluminium bronze the operation is started by introducing a certain quantity of copper through *k*, the anode being then lowered until it touches the copper, which is melted by the passage of the current. Alumina (Al_2O_3) obtained from bauxite (*see below*, Oxide and Hydroxide of Aluminium) is then charged into the furnace, and the anode is raised slowly so that the electric arc between the copper and the carbon passes through the alumina. This melts and gives up oxygen to the carbon of the anode, which is oxidised with formation of CO, and the aluminium formed alloys with the copper. The fused alloy is discharged into the carbon vessel, *t*, where it solidifies in blocks.

When metallic aluminium is to be produced, cryolite is added as a flux in a furnace lined with alumina, and alumina (10 to 20 per cent.) is then gradually added, and rapidly forms molten aluminium. The anode always consists of carbon and the cathode is of iron, but as soon as molten aluminium is formed this acts as a cathode. The molten aluminium, which is formed under a layer of molten material, is extracted every 24 to 36 hours by immersing tubes into the melted mass which syphon off the aluminium from below, or by tapping it through a hole in the bottom, or by removing it in large ladles and then remelting it. The voltage in the bath is 6 to 8, but this increases when the aluminium diminishes, fresh alumina being then added.

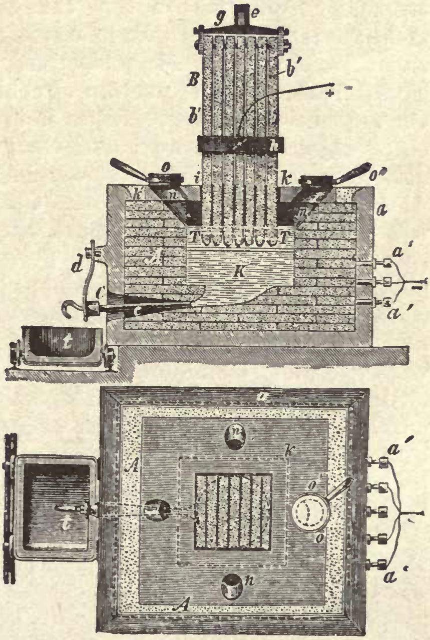


Fig. 278.

The process encountered another difficulty in the impurity of natural alumina, which yielded aluminium containing 2 to 3 per cent. of silicon, and therefore useless. To-day pure aluminium oxide is prepared artificially from bauxite (*see below*, Bayer Process), and thus pure aluminium is obtained which contains only 0·05 per cent. of SiO_2. Since, however, the preparation of pure aluminium hydroxide (99·9 per cent.) has an appreciable influence on the cost of the aluminium, attempts have been made to utilise the cheaper aluminium silicates. Thus, Moldenhauer prior to 1909 and Tone in 1909 obtained sufficiently pure alumina by fusing aluminium silicate with ferric oxide and carbon: $Al_2O_3, 2SiO_2 + 2Fe_2O_3 + 10C = Al_2O_3 + 2Fe_2Si + 10CO$; the application of this process naturally depends on the possibility of utilising all the ferro-silicon (Fe_2Si) formed, as well as the carbonic oxide (1 kilo of Al_2O_3 gives 1·36 kilo of CO).

Until 1905 commercial aluminium had a purity of 98·5 per cent., but now 98·3 to 99·8 per cent. metal of increased resistance to chemical and mechanical agents is obtained by using pure artificial cryolite (*see later*) and electrodes with the least possible proportion of ash.

As regards the purity of the carbon electrodes, the presence of hydrocarbons is not of importance, but mineral impurities are harmful, especially silica, which causes loss of fluorine: $SiO_2 + F_4 = SiF_4 + O_2$. This secondary oxygen also accelerates the wear of the electrodes, and since 1 to 2 kilos of the latter are used up per kilo of aluminium, even small amounts of silica or silicates (ash) falling to the bottom of the bath with the fused aluminium suffice to form an aluminium containing too much silicon. For these reasons use cannot be made as electrode of anthracite or coke, but retort coke (graphite with less than 1 per cent. of ash) or petroleum coke with 0·5 per cent. of ash may be employed; the coke is powdered, made into a paste with 10 per cent. of tar, 4 per cent. of pitch, 3 per cent. of lamp-black, and 3 per cent. of alumina, pressed into moulds under high hydraulic pressure and heated in furnaces to 1150° to burn away all organic matter.

PROPERTIES. Aluminium is a metal of silvery appearance with a specific gravity of 2·64 to 2·70, and melts at 645°. It is ductile and malleable, but more so at about 100°. It is not altered in the air, because it immediately becomes covered with a very thin layer of air and of adherent oxide, which preserves it from atmospheric corrosion. Hydrochloric acid dissolves it easily, and therefore also acetic acid mixed with NaCl, whilst, on the other hand, it is very resistant to the action of cold dilute nitric acid and of sulphuric acid. On account of these properties it is used for the manufacture of tanks and other objects for many industries (cheese factories, fats, eatables, etc.). It dissolves in alkali hydroxides, especially on heating, with evolution of hydrogen: $Al + 3KOH = Al(OK)_3 + 3H$. Compact blocks of aluminium are oxidised with difficulty on heating, whilst when in the form of very thin foil or as fine powder, it is easily set on fire by a gas flame, emitting a very bright light (*aluminium lamp*). If aluminium filings are brought into contact with a solution of mercuric chloride, *aluminium amalgam* is formed, which is a very active reducing agent, and thus immediately evolves hydrogen in contact with water, forming aluminium hydroxide.

If aluminium is employed as an electrode in a voltameter, it only allows an alternating current to pass when it is connected with the negative pole—cathode—whilst if an aluminium plate is allowed to act as anode, it does not let the current pass within certain limits, and on account of this property it is utilised as a " rectifier " for alternating currents.

APPLICATIONS. On account of its physical and chemical properties aluminium gave rise to great hopes that it would be employed on an enormous scale, and it was even supposed that it would replace iron and other metals in common use. Its exceptional lightness, its appearance, and its resistance to atmospheric influences did not, however, suffice to establish its general use as had been hoped, this being due more especially to its lack of hardness. It also easily alters its properties when it contains minimal traces of impurities, such as a trace of sodium, which causes it to be attacked by water. Moreover, it cannot be worked with a file, because it " smears," that is, fills the interstices of the file. Some of these disadvantages can be overcome by suitable additions, such as 2 to 15 per cent. of phosphorus. An important application of aluminium has now been found in *thermit* (*see below*), and it is also used in the form of very thin foil for packages to replace tin foil. In France it is now used for coinage. During 1904 the automobile factory of Rochet and Scheider at Lyons alone used 28 tons of aluminium, in the form of various alloys, for the manufacture of 280 motors. Large amounts of powdered aluminium are used in metallic paints.

A very important application of metallic aluminium is in the manufacture of its alloys, which are largely used. We shall mention the most important of these. *Aluminium bronze* is an alloy of copper containing 3 to 10 per cent. of Al. It has a specific gravity of 8·37 to 7·65, and a golden colour which varies from reddish to bright yellow. When it contains 10 per cent. of Al it melts at 1100°, and is obtained directly in the electric furnace (*see above*), or by pouring Al into molten copper. Its electrical conductivity is 13·6 per cent.

of that of copper. It is very resistant to the action of acids, NaCl, NH_3, S, alkalis, alum, Cl, sulphites, etc.

Aluminium brass is ordinary brass containing 33 per cent. of zinc, to which 0·5 to 4 per cent. of Al is added. It is easily malleable at a dark red heat, and is sometimes used instead of aluminium bronze, but is less resistant to various reagents. *Magnalium* is an alloy of aluminium with less than 2 per cent. of magnesium (often 1 per cent.), and is obtained by adding Al to an electrolytic bath of molten carnallite. Whilst the two metallic components of this alloy have many disadvantages for practical purposes, magnalium enjoys many advantages, and its properties are so useful that they guarantee it a prosperous future. It has a specific gravity of 2·4 to 2·5, is easily melted and cast; it does not smear under the file, has a very fine grain, may be turned in the lathe even at high speed, and may be polished like a mirror. It is used for many parts of machinery, for cooking utensils and scientific apparatus, and as it retains its silvery lustre very well, it is suitable for optical mirrors, etc. It costs about £200 per ton. *Zimalium*, a cheaper alloy of aluminium with a little manganese and zinc, has also been recently prepared.

For many years, and to a certain extent to-day, serious difficulties have been encountered in soldering aluminium. Of the various alloys which are to-day used for soldering, we shall mention only one, patented in 1905, formed of 64 parts of tin, 30 parts of zinc, 1 of lead, and 1 of aluminium. To-day, however, aluminium can be perfectly welded autogenously by the oxy-acetylene blow-pipe (p. 191) by coating the point to be welded if necessary with a thick aqueous solution of potassium chloride, sodium chloride, lithium chloride, and potassium bisulphate, mixed in various proportions in order to prevent oxidation during heating. In order to determine whether other foreign metals are present in a soldered part, M. Schoop in 1907 immersed the soldered portion in water feebly acidified with HCl; hydrogen is evolved at the soldered point only when foreign metals are present.

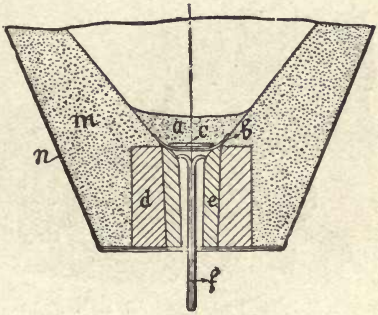


FIG. 279

ALUMINO - THERMIC WELDING. The autogenous welding of metals, that is, the stable, homogeneous union by fusion of two pieces of the same metal without interposition of extraneous metals, has been long carried out in the oxy-hydrogen (*see* p. 190) or oxy-acetylene blowpipe (*see* p. 191), but autogenous aluminothermic welding is in many cases now more economical and more practical; the basis of this is as follows: As long ago as 1827 Wöhler observed the great reducing power of aluminium when this was heated with metallic oxides. Later the heat of formation of alumina was found to be very high: $Al_2 + O_3 = Al_2O_3 + 380$ Cals.; thus each kilo of aluminium burnt or transformed into oxide liberates 7140 Cals. and may generate temperatures above 3000°. If a mixture of aluminium powder with almost any metallic oxide (except MgO) is heated so as to start the reaction of the aluminium with the oxygen of the oxide, the heat liberated is so great that all the metal of the oxide is set free in the fused condition, *e. g.*, $Cr_2O_3 + Al_2 = Al_2O_3 + Cr_2$, or $Fe_2O_3 + Al_2 = Al_2O_3 + Fe_2 + 197$ Cals.

Hans Goldschmidt in 1895 was the first to make practical use of these reactions: (1) to prepare in a very pure state metals such as chromium, manganese, glucinum, calcium, silicon, titanium, thorium, molybdenum, vanadium, nickel, cobalt, etc., which had formerly been obtained less pure or only with the greatest difficulty (Ger. Pat. 96,317); (2) to utilise the formation of pure iron (99·5 per cent.) at a high temperature to effect excellent autogenous welding of articles of wrought-iron, cast-iron, and steel (Ger. Pats. 97,585, 1896; 103,121, 1897; 125,088 and 127,374, 1899; 136,142, 1901, and 174,045, 1904, and corresponding patents in all other countries).

Under the name **thermit**, Goldschmidt placed on the market a mixture of equal parts of iron oxide and granular aluminium. If the temperature at one point of this mass is raised to about 1500° by heating it with a fuse formed of a magnesium wire, which ends in a small sphere of aluminium powder and barium peroxide, and is lighted by means of a match, combustion spreads throughout the mass, and when it ceases, molten iron remains, covered by a layer of molten alumina. By suitable arrangements the very hot molten iron is caused to flow round the objects at the point where the welding is required. Usually the mixture is ignited in a conical crucible or funnel, *m*, made of compressed magnesia (Fig. 279), which withstands a temperature of 3000°, and is surrounded by sheet iron, *n*. The orifice is furnished with replaceable parts, namely, a sheet of asbestos, *b*, an iron plate, *c*, covering the orifice before running out, a ring of calcined magnesia, *d*, carrying a second concentric ring, *e*, also of magnesia, and a rod of iron, *f*, with an enlarged upper extremity like a nail.

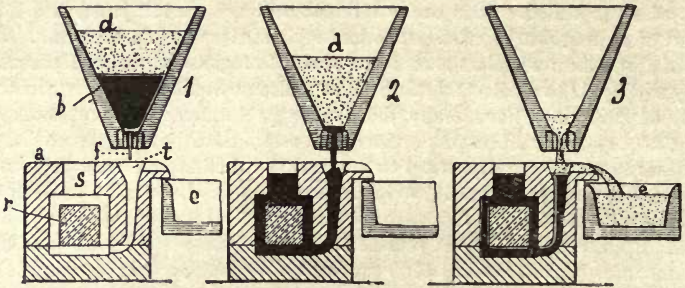


FIG. 280.

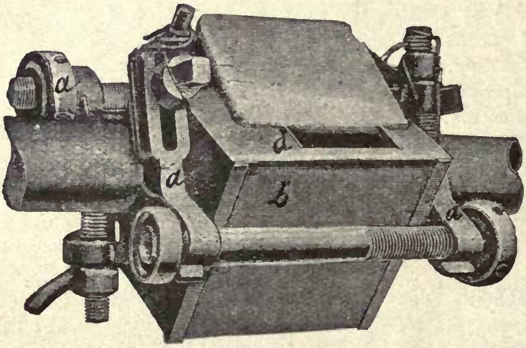


FIG. 281.

Before every operation the crucible and the objects to be welded are heated in a lamp or with hot air to expel moisture. The funnel is then charged with the well-mixed thermit, which is ignited at any point, the cone being then covered with a light asbestos lid. The reaction is finished when the surface of the shining, molten mass shows no black points of non-molten material. The workman charged with running off wears blue or smoked glasses to dull the glare of the fused mass. The moulds which surround the extremities of the pieces to be welded, and into which the molten iron (ferro-thermit) flows, are composed of 60 to 70 per cent. of refractory earth (like that of steel foundries) and 30 to 40 per cent. of yellow clay made into a paste and dried first in the air and then in an oven. Fig. 280 shows the arrangement for welding two pieces of square iron bar, *r*. Phase 1 shows the molten iron in the crucible covered by the fused alumina, *d*; below are the mould, *a*, with the section of the iron bar to be welded, the inlet, *t*, and outlet, *s*, for the molten iron, the side channel of *t* discharging the excess of molten iron and the fused slag into the vessel, *e*. Phase 2 shows the iron after the rod, *f*, has been removed, and Phase 3 the discharge of the alumina into the vessel, *e*.

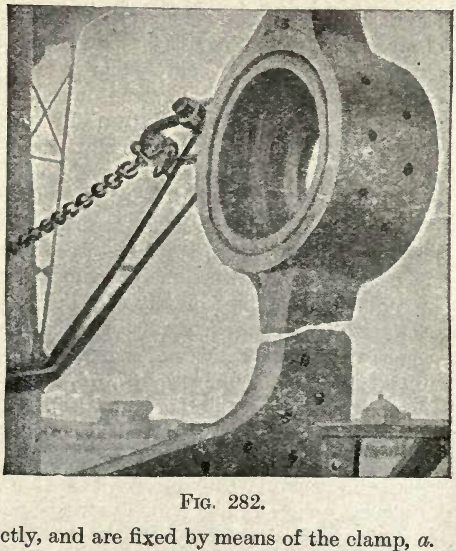


FIG. 282.

Fig. 281 shows the arrangement for joining two iron tubes, the extremities of which are well cleaned and filed so as to fit exactly, and are fixed by means of the clamp, *a*. The point to be welded is enclosed in the clay mould surrounded by a sheet-iron box, *b*, the joints being closed with a layer of moist sand 2 to 3 cm. thick; after the whole is dried and heated with hot air, the molten iron flows from the funnel into the orifice, *d*.

Fig. 282 represents a ship's broken stern post, and Fig. 283 shows the same mended by alumino-welding and left still in the rough. The heating occupied three hours before the mouth of the mould became red-hot, molten iron from about 600 kilos of thermit then flowing in in a few minutes; cooling lasts about twenty-four hours.

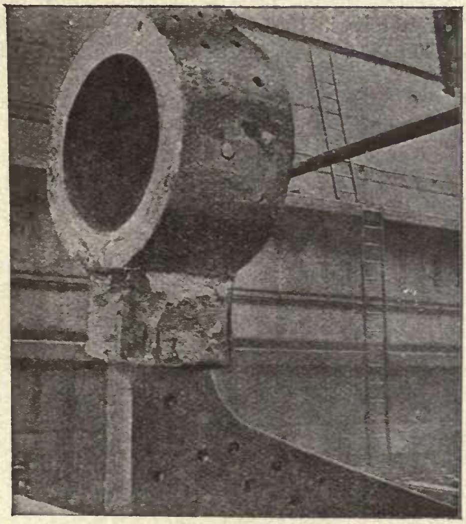


Fig. 283.

One of the commonest uses of alumino-welding is in the welding of railway and tramway rails *in situ* so as to form miles of continuous rails; by this means the wear on the ends of the rail-lengths and the jump of the carriages are avoided. Fig. 284 shows the practical arrangement for welding rails. In 1911 about 500,000 rail-weldings were carried out in various countries, 25,000 in Italy (9000 in Milan). One of the great advantages of alumino-welding lies in the possibility of repairing large machine parts without moving them; such repairs, often costing hundreds of pounds and occupying months, are now

Fig. 284.

executed in a few days or a few hours and at minimum expense. Prior to the European War thermit cost about 2*s.* 5*d.* per kilo.

STATISTICS AND PRICES. Whereas up to a few years ago there were in existence only two or three aluminium factories, these are now numerous and important.[1]

The world's output of aluminium in 1880 was 2 tons, in 1885 13 tons, in 1888 39 tons, in 1890 175 tons, in 1893 716 tons, in 1896 1790 tons, in 1898 4024 tons, in 1900 7743 tons, in 1905 11,500 tons, in 1908 18,000 tons, in 1910 34,000 tons, in 1911 45,000 tons, in 1912 60,000 tons (almost one-half in America), and in 1913 72,000 tons. The production has since increased rapidly, especially in the United States.

The consumption of aluminium in different countries is as follows (tons):

	1901	1906	1910	1911	1912
United States and Canada	3,200	5,600	21,600	22,000	28,000
France	900	2,600	5,400	5,000	6,000
England	600	1,000	2,700	3,000	4,000
Italy	—	—	900	900	1,000
Germany, Austria, Switzerland, Russia, etc.	3,000	5,300	13,500	17,000	22,100

The production in different countries is as follows (tons):

	1902	1907	1910	1911	1912	1913	1914	1915	1916
United States .	3,000	7,500	16,100	20,000	25,000	29,500	—	—	—
Canada . .	—	—	3,500	4,000	8,300	5,916	—	—	—
France . .	1,400	6,000	9,500	10,000	13,000	15,000	—	—	—
Germany, Switzerland and Austria	2,500	4,000	8,000	8,000	12,000	16,000	—	—	—
England . .	600	1,800	5,000	5,000	7,500	10,000	—	—	—
Norway . .	—	—	900	900	1,500	2,500	—	—	—
Italy . . .	—	—	800	800	800	875	937	904	1126

In Italy the manufacture of aluminium was only started in 1906 at Bussi in the Valle di Pescara by treating the bauxite of Lecce nei Marzi (5100 tons in 1910); in 1908 3 series of small furnaces were working, comprising 50 furnaces in all, and produced 600 tons of aluminium; in 1911 a fourth series of furnaces was at work. Bauxite deposits have recently been discovered on the left bank of the Liri. In 1907 Italy imported 538 tons of aluminium and its alloys, in 1908 442 tons, in 1909 490 tons, and in succeeding years as follows (tons):

	1911	1913	1914	1915	1916	1917
Crude aluminium .	213	102 (£7,320)	74	1621	1977	3799
Sheet, rod, tubes . .	263	293 (£30,480)	160	25	103	144
Wire	4	9 (£840)	3	1	1	1
Made articles . .	50	78 (£17,180)	75	18	51	52

The total value of the aluminium imported in 1917 exceeded £1,760,000.

France in 1904 produced 1500 tons of aluminium and exported 306 tons in 1901, 662

---

[1] *In France*—

	Share capital £	Available hydraulic power H.P.
Société électrometallurgique française, with works at Froges, at Prace, at Saussaz (near St. Michel de Maurienne) and at Argentière-la-Bassée	600,000	65,000
Compagnie des produits chimiques d'Alais, with works at Calypso, St. Felix, and St. Jean-de-Maurienne	420,000	40,000
Société d'électrochimie (makes chlorate also)	240,000	10,000
Société des forces motrices et Usines de l'Arve	160,000	13,000
Société des produits électrochimiques et électrometallurgiques des Pyrénées	—	12,000
Switzerland—		
Industrie A. G. Neuhausen, with works at Neuhausen, Reinfelden, Lend-Gastein, Lend-Rauris, and Chippis	1,240,000	74,000
America—		
Aluminium Co. of America, with works at Niagara Falls (50,000 h.p.), Massena (40,000 h.p.), and Canada (8000 h.p.)	4,000,000	98,000
Italy—		
Societa italiana per la fabbricazione dell'alluminio	1,200,000	5,000

in 1903, 1470 in 1906, 4400 in 1909, 4181 in 1911, 1684 in 1913, 1501 in 1914, and 415 in 1915.

Germany imported 1090 tons of aluminium in 1901 and 9890 in 1910, and exported 282 tons in 1901 and 616 in 1910.

Switzerland exported 504 tons of aluminium in 1901, 722 in 1908, 1652 in 1909, and 3649 in 1910.

The change in price of aluminium illustrates the history of the industry very effectively. In 1855 1 kilo of aluminium cost £50, in 1857 £12 (*see* p. 724), in 1874 £8, in 1886 £3 8*s*., in 1890 12*s*., in 1895 3*s*. 2½*d*., in 1902 2*s*.; in 1906 it rose to 3*s*. 7*d*. per kilo on account of the large demand, and in 1909 it fell again to 1*s*. 2½*d*. and to 1*s*. 5*d*. in 1910 on account of the large production by the older and newer works, which attempted to form an international trust in 1909 in order to raise the price, but did not succeed in coming to an agreement. In spite of the present low price, the Aluminium Gesellschaft of Neuhausen in Switzerland has paid the following dividends to shareholders: 16 per cent. in 1904, 18 per cent. in 1905, 22 per cent. in 1906, and 26 per cent. in 1907.

Aluminium powder (for photographic lamps, crackers, paints, etc.), cost 2*s*. per kilo in 1913.

ALUMINIUM COMPOUNDS

ALUMINIUM OXIDE: Al_2O_3 (Alumina). In nature this occurs as *ruby, sapphire, corundum,* and *emery,* which are very hard and have a specific gravity of about 3·9. Rubies and sapphires may be prepared artificially by melting alumina with lead oxide at a red heat in a porcelain capsule. The lead aluminate first formed decomposes by acting on the silica of the capsule and deposits crystals similar to those found in nature, which are coloured ruby red if a little potassium bichromate is added to the fused mass, or blue if a little cobalt oxide is introduced.[1]

Amorphous Al_2O_3 is obtained by heating aluminium hydroxide or other compounds. It is soluble in acids, but if it has been previously heated to redness for some time it becomes insoluble, and the only way then of obtaining it in solution is to fuse it with potassium carbonate or potassium bisulphate.

The industrial preparation of pure aluminium oxide has to-day acquired great importance, as it forms the prime material for the manufacture of aluminium (*see above*) and aluminium sulphate (*see later*). It is obtained from cryolite and to a larger extent from bauxite, in various ways. According to Bayer's process, the bauxite, $Al_2O(OH)_4$,[2] is calcined

---

[1] **Artificial Rubies.** Of the various methods of manufacture, the most recent, Verneuil's process, deserves mention. A solution of aluminium sulphate containing iron as an impurity is mixed with one of chrome alum and precipitated with ammonia; the precipitate is first dried in the air, then raised to a cherry-red heat, and finally melted in the oxy-hydrogen flame. Drops weighing about 20 grms. and 1·5 cm. in diameter are removed from the molten mass and allowed to solidify; all gradations of colour are so obtained varying with the quantity of chrome alum which was added. About 1 ton of artificial rubies is manufactured yearly.

In 1894 Verneuil published his process, with which 7000 to 10,000 carats are made per day for watches and electrotechnical purposes. In 1910 the electrochemical works at Bitterfeld (Germany), with 200 furnaces, prepared daily 4000 carats of artificial rubies which cannot be distinguished from the natural stones; in 1912 the price of artificial rubies fell so low as to render their manufacture unremunerative.

[2] The question whether there are important deposits of bauxite in Italy has been discussed for some time, but until a short time ago it was almost unknown. Recent researches of Mattirolo and analyses by Formenti have, however, proved the presence of notable surface deposits (1,000,000 sq. metres of a thickness of 3 metres) at Lecce nei Marzi on the slope of Monte Turchio. This bauxite contains 50 to 55 per cent. of aluminium and 3 to 4 per cent. of silica (SiO_2), but the content of iron sometimes exceeds 25 per cent. of Fe_2O_3, and this explains how the engineers of the Bureau of Mines erroneously classified these minerals as iron ores. They are now the property of the Società italiana per la fabbricazione di alluminio, who treat and purify these ores in their works at Bussi.

Crude Bihar bauxites contain about 1·5 per cent. SiO_2 (sometimes more), 2 to 3 per cent. TiO_2, 53 to 58 per cent. Al_2O_3, 28 to 30 per cent. Fe_2O_3 (sometimes much less), 10 to 15 per cent. H_2O, and traces of CaO and MgO.

The output of bauxite in the United States was 53,000 tons in 1908, 131,000 in 1909, 151,000 (£144,000) in 1910, and 160,000 in 1911, most coming from Arkansas; the price at the mine was about £1 1*s*. per ton. The United States import marked quantities of French bauxite, which and pulverised, mixed with a little lime and then treated with a sodium hydroxide solution of 45° Bé. at a pressure of 3 to 4 atmospheres. (Bauxite for the manufacture of aluminium should not contain more than 0·2 per cent. of silica.) Sodium aluminate soluble in water is thus obtained. It is filtered hot and washed, and to the clear solution after suitable dilution about two-thirds of pure gelatinous aluminium hydroxide is added. The whole is then stirred continuously in large vats for 5 to 6 days, after which time all the sodium aluminate is dissociated and all the alumina precipitated in the pure state, together with that originally added. It is separated in a filter-press and all the sodium hydroxide then remains in solution and is re-utilised (*see also* Fr. Pat. 373,070 of 1906). Formerly a current of CO_2 was passed into the sodium aluminate solution and this first precipitated pure aluminium hydroxide and afterwards the silicates, whilst a solution of sodium carbonate remained which was re-utilised in the process. An excess of sodium hydroxide is more effective in preventing the precipitation of silica. The hydroxide obtained by the Bayer process is free from iron and silica, contains 40 per cent. of water, and after drying forms a white powder consisting of the oxide, Al_2O_3.

Pure alumina is also prepared in the electric furnace by mixing powdered bauxite with coal, and with a flux, such as Na_2CO_3, cryolite, or calcium fluoride, and also sometimes Al and Fe_2O_3 (a borate is still more effective; Ger. Pat. 205,790 of 1908). All the impurities collect as a slag in the very fusible alloy of aluminium and iron or iron silicate which is easily separable.

When aluminium oxide is heated in a current of chlorine in presence of carbon it forms aluminium chloride, $AlCl_3$. Refined anhydrous alumina of 98 to 99 per cent. in the form of a heavy powder costs £40 per ton, whilst in the form of a light powder it costs £84.

ALUNDUM is alumina which has been fused, and is obtained by heating pure bauxite in the electric furnace. Formerly the Norton Company obtained abrasive materials (diamantine) in this way, but since its melting-point is about 2000°, this material is used to make infusible laboratory apparatus (crucibles, muffles, tubing and furnace parts). The purest quality is white, and contains only 1 per cent. of impurity; the reddish-brown quality contains 6 to 8 per cent. Its thermal conductivity is double that of porcelain and quadruple that of baked clay; its hardness on the Mohs' scale is 9 to 10 and its specific gravity about 4. It is but little attacked by dilute acids, alkalies or fused alkali carbonates. The material is porous and may be used directly for Gooch crucibles. It is a better electrical insulator than porcelain, even at a high temperature; its coefficient of linear expansion is 0·0000059–0·0000085. In 1913 the world's output of alundum as an abrasive was 5000 tons.

ALUMINIUM HYDROXIDE: $Al(OH)_3$. As already noted above, this compound occurs in nature as *diaspore, bauxite,* and *hydrargillite.* It is obtained as a gelatinous mass by treating a soluble aluminium salt with NH_3, alkali hydroxide, or alkali carbonate: $2AlCl_3 + 3CO_3Na_2 + 3H_2O = 2Al(OH)_3 + 3CO_2 + 6NaCl$. The hydroxide is soluble in NaOH, but not in NH_3 (*see below*). It is prepared industrially by Löwig's process, by treating a solution of sodium aluminate with milk of lime:

$$2AlO_2Na + Ca(OH)_2 = 2NaOH + (AlO_2)_2Ca.$$

The dissolved sodium hydroxide is utilised again for the preparation of sodium aluminate, whilst the precipitated calcium aluminate is dissolved in HCl:

$$(AlO_2)_2Ca + 8HCl = CaCl_2 + 2AlCl_3 + 4H_2O.$$

On then mixing the solution of $AlCl_3$ with calcium aluminate in the exact proportions indicated by the following equation, pure aluminium hydroxide is precipitated:

$$2AlCl_3 + 3(AlO_2)_2Ca + 12H_2O = 8Al(OH)_3 + 3CaCl_2.$$

---

scheaper in spite of a Customs' duty of 4*s*. per ton; in 1908 the imports were 22,000 tons, in 909 19,000 tons, and in 1910 16,000 tons (£13,120).

In 1911 Italy produced 5690 tons of bauxite, in 1915 5900 tons (£3304), and in 1916 8887 tons.

In 1917 important deposits of bauxite were discovered in Spain (Barcelona), these containing 1 to 3 per cent. of insoluble silica, 5 to 10 per cent. soluble silica, 62 to 68 per cent. Al_2O_3, 5 to 7 per cent. Fe_2O_3, 2 to 5 per cent. TiO_2, 0·2 to 0·6 per cent. CaO, 0·2 per cent. MgO, 0·4 to 0·8 per cent. Na_2O, 0·1 to 0·2 per cent. K_2O; loss on ignition, 13 to 15 per cent.

Besides for making aluminium and various aluminium salts, bauxite serves for making alundum (*see* above) and firebricks.

In 1909 the output of bauxite was as follows: United States, 131,000 tons; France, 130,000; Italy, 3900, and England, 10,000 tons.

The purification of bauxite has also been described in the preceding pages.

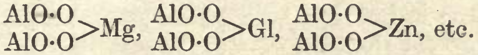
The freshly precipitated hydroxide can be dissolved in a solution of aluminium chloride or acetate, and on then subjecting this solution to dialysis (p. 106) the chloride or acetate diffuses through the membrane, whilst a colloidal aqueous solution of the hydroxide remains. This has a slight alkaline reaction and is coagulated by traces of acids, alkalis, or salts.

Freshly precipitated aluminium hydroxide dissolves in acids and in alkali hydroxides, forming *aluminates*, $AlO\cdot ONa$; when the hydroxide is dried it no longer dissolves in acids.

The aluminates may be considered as derivatives of **Aluminium metahydroxide**, $AlO\cdot OH$, which is formed by heating the ordinary hydroxide cautiously until one molecule of water is eliminated. If a soluble salt of the alkaline earth metals, magnesium, etc., is added to the aqueous solution of an alkali aluminate, a precipitate of the aluminate of calcium, magnesium, etc., is formed:

$$2AlO\cdot ONa + CaCl_2 = 2NaCl + (AlO\cdot O)_2Ca.$$

Various crystalline minerals, known as *spinels*, are found in nature, which correspond in constitution with these aluminates, for example:



$$\begin{matrix}AlO\cdot O\\ AlO\cdot O\end{matrix}{>}Mg,\quad \begin{matrix}AlO\cdot O\\ AlO\cdot O\end{matrix}{>}Gl,\quad \begin{matrix}AlO\cdot O\\ AlO\cdot O\end{matrix}{>}Zn,\ \text{etc.}$$

Aluminium hydroxide behaves both as a weak base and as a weak acid, so that it is able to form salts both with strong acids and with strong bases.

Thus freshly precipitated $Al(OH)_3$ dissolves in NaOH or in HCl, but the salts are not very stable and are already decomposed by carbon dioxide or ammonium chloride with precipitation of the hydroxide. Salts which are formed with strong acids have an acid reaction in aqueous solution, and those formed with strong bases have an alkaline reaction, because they are in part *hydrolytically dissociated* by water in a similar manner to any other salts of strong acids with weak bases or weak acids with strong bases. Their general behaviour is explained by hydrolytic dissociation due to the ionisation of minimal traces of water into $H^{\cdot}$ and OH'.

In the salts formed from weak bases and strong acids in aqueous solution some of the cations unite with a few OH' anions of ionised water forming neutral molecules, and the free $H^{\cdot}$ cations of the water thus remain and produce an acid reaction. The OH' anions having disappeared, other molecules of water are ionised and further cations of the salt are hydrolysed, thus increasing the acid reaction until a certain equilibrium is reached. In the case of salts formed of strong bases with weak acids, their aqueous solution has an alkaline reaction, because some of their anions are hydrolysed with the $H^{\cdot}$ cations of the ionised water molecules, and OH' anions of the water are liberated, which impart the alkaline reaction to the solution. The strong alkaline reaction of sodium and potassium carbonate (p. 546) is thus explained, as their aqueous solutions are strongly hydrolysed.

When sodium carbonate or ammonium sulphide is added to a solution of an aluminium salt aluminium hydroxide is precipitated instead of the carbonate or sulphide as occurs in the case of various other salts; chromium salts behave similarly. This apparent abnormality is logically explained by the instantaneous hydrolysis of the carbonate or sulphide of aluminium (or chromium) which occurs at the instant of their formation in presence of much water, because, being formed of a very weak base and very weak acids (H_2CO_3 and H_2S), they are completely hydrolysed by excess of water with evolution of CO_2 or H_2S and separation of gelatinous aluminium hydroxide.

Freshly prepared aluminium hydroxide precipitates many dyestuffs (alizarin and anthracene dyestuffs) from their solutions, forming insoluble combinations of various colours, which are called *lakes*. This reaction is utilised with the help of solutions of aluminium acetate or of sodium aluminate, for mordanting fabrics by impregnating them with these solutions. On heating, the acetate is then decomposed with formation of acetic acid, and aluminium hydroxide remains in the fibre. On then immersing the fabric in a bath containing the dyestuff, the colour is fixed in the tissues through the formation of these lakes.

Waterproof fabrics are obtained by impregnating the materials with aluminium acetate and then heating them. All the pores of the fibres are thus filled with the gelatinous hydroxide, which is then transformed into insoluble aluminium oxide. The fabrics lose all their capillary and are no longer wetted by water.

STATISTICS AND PRICES. Commercial aluminium hydroxide in paste form costs £10 per ton; the dry substance in powder costs £40 per ton; sodium aluminate in solution (25° Bé.) costs £18, and the solid with 40 per cent. of Al_2O_3, £28 per ton; commercial aluminium acetate in solution (10° to 12° Bé.) costs £9 4*s*. per ton, and of 14° to 15° Bé. £14. Bauxite of good quality costs £2 to £2 8*s*. per ton, and Germany (which does not produce bauxite) imported 39,325 tons in 1905 and 44,000 in 1909. The purest product is used for the manufacture of aluminium and the least pure for the production of refractory materials. In 1908 Italy produced 7000 tons of bauxite, of the value of £2520, and in 1902 imported 420·4 tons of aluminium hydroxide, of the value of £4040; in 1907 390 tons, in 1908 360 tons, in 1909 455 tons, of the value of £4360, in 1910 365 tons, and in 1911 527 tons (£7377). France possesses the largest bauxite deposits in the world, especially in the Department of Var; in 1907 it produced 430,000 tons of bauxite and in 1908 191,000 tons, and in 1907 it exported 110,000 tons, of the value of £88,000, 81,782 tons in 1911, and only 72,330 in 1912. Austria imported (from Germany) 2657 in 1905, 3160 tons in 1906, 4840 in 1907, and 3670 tons in 1908, of the value of £40,000. The United States of America produced 48,130 tons of bauxite in 1906, of the value of £48,000, in 1913 215,000 tons at £1 per ton at the mine, and in 1917 569,000 tons, of which 507,000 tons were supplied by the Arkansas deposits; in 1916 the United States imported 30 tons of bauxite and in 1917 7760 tons. England produced 9500 tons in 1909, 3792 in 1910, 9500 in 1916, and 13,000 in 1917.

ALUMINIUM CHLORIDE : $AlCl_3$. This substance is prepared either by passing a current of dry gaseous HCl over fragments of aluminium heated in a porcelain tube, or by heating Al_2O_3 and carbon in presence of chlorine. The chloride which distils condenses as a white crystalline mass of hexagonal scales which are deliquescent and very hygroscopic. It is easily hydrolysed by water, and in order to maintain it in solution without separation of $Al(OH)_3$ it is therefore necessary that a little HCl should be present. On concentrating the aqueous solution by heating it is easily hydrolysed with evolution of HCl and separation of the hydroxide. One method of carbonising wool is based on this reaction. Wool is carbonised in order to destroy the vegetable residues which are found mixed with it, and this is effected by aluminium chloride, because whilst wool itself resists the moist HCl vapours at 120° quite well, the straw and cotton are attacked and carbonised or incinerated. Ordinarily, however, dilute sulphuric acid is used for carbonisation. When aluminium chloride is pure it fumes in the air and boils at 183°. At 440° its vapour density corresponds with the formula Al_2Cl_6, whilst at 760° it corresponds with $AlCl_3$. It is soluble in water, alcohol, and ether. A solution of $Al(OH)_3$ in HCl is used as a disinfectant. Certain double salts of little importance are also known:

$$AlCl_3,NaCl;\ AlCl_3,PCl_5,\ \text{etc.}$$

A commercial solution of $AlCl_3$ of 30° Bé. costs £10 per ton. The anhydrous solid costs £58 per ton.

ALUMINIUM AND SODIUM FLUORIDE (*cryolite*) **: $AlF_3,3NaF$.** This mineral forms large banks at Ivigtut near Arkus Fjord (Greenland) and is translucent-white in colour, brittle and of crystalline structure, its hardness being about 3 and its density 3. It melts easily when heated and yields HF when treated with concentrated sulphuric acid. If pure, it contains 51·4 per cent. F, 32·8 per cent. Na, and 12·8 per cent. Al. Cryolite was studied in 1850 by Julius Thomsen with a view to the manufacture of soda and alumina, and in 1859 the first cryolite soda factory was started at Oeresund near Copenhagen, this being followed by others at Pittsburg, Mannheim, Hamburg, Prague, and Warsaw. With the extension of the Solvay soda process after 1880, these factories were gradually closed, and the principal use of cryolite at the present time is in the making of enamels (*see later*). It is also employed in aluminium works as a flux and should then contain less than 0·2 per cent. of quartz, otherwise silicon separates in the electric furnace and this renders the aluminium brittle; smaller quantities of cryolite are used for making porcelain glasses.

Artificial cryolite is now prepared by mixing aluminium hydroxide with hydrofluoric acid solution obtained by distilling CaF_2 (free from silica) with H_2SO_4 and neutralising with soda (Ger. Pat. 35,212). Hulin dissolves aluminium hydroxide in excess of hydrofluoric acid, this giving first $Al_2F_6,6HF$; neutralisation of the latter with sodium peroxide results in separation of insoluble cryolite, pure hydrogen peroxide remaining in solution. Loesekann (Ger. Pat. 205,209) prepares artificial cryolite by heating in a furnace a mixture of $CaF_2 + K_2SO_4 + 4C$, which gives $CaS + 2KF + 4CO$; the readily soluble KF is extracted with water and treated with Na_2SO_4 solution, slightly soluble NaF then separating and the K_2SO_4 being regenerated; the reaction, $12NaF + Al_2(SO_4)_3 = 3Na_2SO_4 + 2(AlF_3, 3NaF)$, then yields cryolite, which is pure even if the calcium fluoride were impure, since silicon fluoride cannot form (U.S. Pat. 957,754, 1910). Artificial cryolite is now prepared for making pure aluminium.

The cryolite field of Ivigtut is 170 metres long, 60 metres wide, and more than 10 metres deep, and the mineral dug out with pickaxes is sent to Copenhagen, where the white pieces are sieved off and the rest broken up and powdered and separated into different degrees of fineness by means of sieves provided with magnets to remove the carbonate of iron, blende, copper and iron pyrites and lead sulphide present as impurities.

In 1907 Greenland produced 13,150 tons of cryolite, all utilised and sold by the Oeresund Chemiske Fabriker of Copenhagen, which in 1913, of an output of 7760 tons, sent 1855 tons to France, 1508 to Germany, 818 to Austria, 1000 to England, 690 to Russia, 660 to Switzerland, 361 to Norway, 318 to Belgium, 219 to Italy, 87 to Sweden, 85 to Spain, 62 to Japan, and 46 to Holland; in Denmark 38 tons were utilised.

ALUMINIUM NITRIDE : AlN. This was first prepared by S. W. Mallet and was later manufactured industrially by Serpeck to obtain ammonia by utilising atmospheric nitrogen (*see* p. 367). It forms white crystals of sp. gr. 3·18 (if impure it is yellow or blue) and is attacked only very slightly by halogens and not at all by HCl, which may be used to remove impurities from the nitride; even if the latter contains metallic aluminium, this is eliminated by gaseous HCl. It is decomposed completely only after prolonged heating at 100° with water, or better by boiling it with 20 to 30 per cent. sulphuric acid solution; even in the cold the moisture of the air produces a little ammonia. Reducing agents (H, C, etc.), do not attack it, but oxidising agents decompose it with formation of alumina. It is an excellent electrical and thermal insulator.

ALUMINIUM SULPHATE : $Al_2(SO_4)_3 + 18H_2O$

Large quantities of this compound are now consumed for purifying waters by filtration (*see* p. 235) and for purifying effluents (p. 249). Much is also used by paper-makers in conjunction with resin for sizing to prevent the ink from spreading; large amounts are further employed in dyeing, in making lakes, in tanning hides, and in making waterproof fabrics. That used in paper-making should be pure, and should not contain more than 0·05 per cent. of iron, whilst that for dyeing with alizarin dyes should contain less than 0·01 per cent. of iron.

The processes of purifying aluminium sulphate are so complicated and laborious that almost all the manufacturers now prepare the salt from highly purified raw materials, namely, sulphuric acid free from iron and aluminium hydroxide obtained by the Bayer process (*see* p. 731). The sulphuric acid of about 60° Bé. is heated to 100° in a copper (or enamelled) vessel, the calculated quantity of pure dry aluminium hydroxide being added a little at a time and the mass stirred slowly meanwhile. The reaction is finished when further addition of the aluminium hydroxide fails to produce frothing. The hot mass is then discharged into leaden pans 15 to 20 cm. deep, in which it is stirred for a time; when it has solidified, and while still hot, it is cut into regular lumps, which afterwards harden completely and are ready for despatching.[1] The product contains about 50 per cent. of water (theoretically 48·6 per cent.) and about 14 to 14·5 per cent. Al_2O_3, and it dissolves entirely in water, giving an acid solution. To detect free sulphuric acid in the sulphate, the concentrated solution is treated with ammonium sulphate and alcohol which precipitate ammonium alum, the filtrate being titrated for free acid.

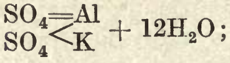
In order to obtain the purest product, free from acid, it is redissolved in hot water and the aluminium sulphate allowed to crystallise in scales; its sp. gr. is 2·71. It is far more soluble than potash alum in water: 100 parts of water at 0° dissolve 86·8 parts and at 100° about 1132 parts of aluminium sulphate.

The dilute aqueous solution is partly dissociated hydrolytically and hence has an acid reaction. When heated to redness the anhydrous sulphate is decomposed into SO_3 and Al_2O_3. The aqueous solution, when treated with an insufficient quantity of NH_3, separates a basic sulphate, $Al_2\left\{\begin{matrix}(OH)_4\\ SO_4\end{matrix}\right. + 7H_2O$ (*aluminite*).

STATISTICS AND PRICES. *See later.*

Lately the price of aluminium sulphate has fallen somewhat—to £4 16*s.* to £6 per ton—and it may therefore be employed in place of alum as a mordant in the dyeing of alizarin and anthracene colours, but it must be free from iron, as otherwise this forms dark violet lakes which deaden the other shades; it may also be used for tanning hides, for hardening cardboard, purification of water, etc.

Aluminium sulphate unites with the alkali sulphates to form double salts which crystallise in large octahedra or cubes and are called *alums*, such as potash alum, $Al_2(SO_4)_3,K_2SO_4 + 24H_2O$; there are many such alums, as the potassium sulphate may be replaced by the sulphates of other monovalent metals, Na, Rb, Cs, Tl, and NH_4, and, on the other hand, Al may be replaced by other trivalent metals, such as Fe, Cr, V, Mn, Co, Ti, etc. Thus, there is an iron potash alum, $Fe_2(SO_4)_3,K_2SO_4 + 24H_2O$; a chrome sodium alum, $Cr_2(SO_4)_3,Na_2SO_4 + 24H_2O$, etc. All these alums are isomorphous (p. 115) and form mixed crystals in any proportions (p. 116), and since they are differently coloured (chrome potash alum has a violet-red colour and iron alum a deep violet colour) they may be superposed in the same crystal, forming variously coloured layers. The constitution of alum may be most simply represented by the following formula:



$$\begin{matrix}SO_4=Al\\ SO_4<K\end{matrix} + 12H_2O;$$

in aqueous solution, however, the alums have no characteristic ions of their own, but show the reactions of the component salts (aluminium sulphate and potassium sulphate), so that they must be considered as true double salts (p. 274), and not as complex salts, like potassium ferrocyanide, ferricyanide, etc. (*see* Iron).

Potash Alum, $Al_2(SO_4)_3,K_2SO_4 + 24H_2O$, is called *common alum*, and is prepared at Tolfa, near Rome, from an abundant mineral, *alumite*, which is a basic alum, $(SO_4)_2AlK,Al(OH)_3$. This is first roasted at 500° and then

---

[1] It may be obtained directly from bauxite (not too impure) as follows: The finely powdered bauxite is mixed with soda and heated to bright redness, the mass being afterwards dissolved in boiling water to give a solution of 35° to 36° Bé. (in the hot); this is filtered, steam and CO_2 (150 to 160 kilos per 150 kilos of Al_2O_3, *i. e.*, per ton of the sulphate) being then passed into the filtrate, which is kept at 60° to 90°. The aluminium hydroxide thus precipitated is collected on a filter, and after washing contains 40 per cent. of Al_2O_3, 2 per cent. Na_2CO_3, 0·035 per cent. Fe_2O_3, and 57 per cent. H_2O. This hydroxide is dissolved in the calculated quantity of pure iron-free sulphuric acid (66° Bé.) heated to 100°, the sulphate being discharged as described above.

extracted with hot water, when the hydroxide remains undissolved. On concentrating and cooling the solution, pure *Roman alum* crystallises in cubes. Alum is also prepared from cryolite and from bauxite or from aluminium silicate with H_2SO_4, a solution of potassium sulphate being added to the aluminium sulphate solution which is so obtained, and the alum then allowed to crystallise. In the province of Sivas (Turkey) there are alum deposits, and from the Gaynyk quarries 3000 tons per annum are extracted.

Potash alum dissolves in 10 parts of cold water or in 0·75 part of boiling water, and shows an acid reaction as it is hydrolysed (p. 271). Alum heated to 120° loses water and forms *burnt alum* as a white voluminous mass.

Alum is used for the same purposes as were mentioned for aluminium sulphate; it is also employed in medicine and for hardening plaster of Paris.

STATISTICS. Commercial crystallised alum costs £8 per ton; the refined product, free from iron, costs £14, burnt alum £24, and Roman alum £30. Chrome alum and commercial iron alum cost about £16 per ton.

The Italian statistics for aluminium sulphate are as follows (tons):

	1909	1910	1912	1913	1914	1915	1916	1917
Output	2750	2773	2727	3308	3229	2094	—	—
Imports (including a little alum)	1647	1774	2556	2570	2602	2441	1555	642

The production and exportation of alum in Italy are as follows (tons):

	1909	1910	1912	1913	1914	1915	1916	1917
Production . . .	2900	2510	1299	1009	1307	1329	—	—
Exportation . . .	392	570	50	1870	1432	59	78	186

Germany produced 4460 tons of alum and 3100 of aluminium sulphate in 1890, 4500 and 50,000 tons respectively in 1902, and about 60,000 tons of the sulphate in 1912; in 1908 28,600 tons of the sulphate were exported.

The United States produced 90,000 tons of aluminium sulphate, of the value £368,000, in 1908, 105,000 tons in 1909, and 105,000 in 1910; 7000 tons of alum were exported in 1908 and 8250 (£60,000) in 1910.

Austria consumed 12,000 tons of aluminium sulphate in 1909.

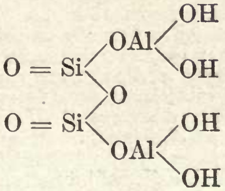
France exported the following quantities of aluminium sulphate: 246 tons in 1913, 208 in 1914, and 6416 in 1915.

England exported 11,000 tons of aluminium sulphate in 1909 and 13,000 (£56,000) in 1910.

The price of aluminium sulphate before the European War was £4 per ton and that of the pure iron-free salt £6 (in Italy).

ALUMINIUM SILICATE (KAOLIN, CLAY)

CERAMIC INDUSTRY. Various double silicates of aluminium and the alkali metals occur abundantly in nature in the various rocks: *leucite*, $(SiO_3)_2AlK$; *albite*, $(SiO_3)_2AlNa, SiO_2$; and *orthoclase* or *felspar*, $(SiO_3)_2AlK,SiO_2$. On exposure of these rocks rain water removes alkali silicates and large deposits of aluminium silicate are formed which, when pure and white, is known as *kaolin*, this being a pure aluminium silicate, $Al_2O_3,2SiO_2 + 2H_2O$, or:



When impure and transported to some distance from the original rock it is coloured brown by various iron oxides and forms *common clay*, which is one of the principal constituents of the soil.[1] Pure, finely divided clay possesses marked plasticity, that is, it has the property of taking up much water to form a paste capable of being moulded, which becomes very hard and contracts to the extent of 20 to 40 per cent. on baking in suitable furnaces and melts if the temperature is sufficiently high. After baking, it has lost all plasticity even when powdered very finely. Clay and kaolin constitute the prime materials of the ceramic industry for the manufacture of bricks, earthenware, and porcelain. However, apart from plasticity, they should be refractory to a high degree, that is, they should resist the action of heat without melting, because in order to render the porcelain hard and compact, they must be heated to very high temperatures.[2] Kaolin for porcelain manufacture should not become

---

[1] A special variety, smectitic clay, constitutes the so-called *Fuller's earth*, which is brownish-grey, is subdivided by water instead of forming a plastic mass, and has the property of absorbing fatty matters with avidity. It is used in large quantities to decolorise oils (*see* Oils, Vol. II., "Organic Chemistry"), the colloidal constitution being first destroyed by heating it above 130°, but not beyond 200°, since then it loses its water of hydration and no longer decolorises. It consists of aluminium and magnesium hydrosilicate, and occurs abundantly in England (Surrey, Kent, Bedford), Saxony (Rosswein), Silesia (Riegersdorf), Vaels (near Aquisgrana), Styria (Cilli), and Italy (Monte Amiata and Montagnola, Sienna). In common use is a variety found in abundance in 1893 in Florida (*Florida earth*), this containing 5 to 24 per cent. H_2O, 40 to 70 per cent. SiO_2, 7 to 35 per cent. Al_2O_3, 0·7 to 5 per cent. MgO, and 0·5 to 7 per cent. CaO. The output of Fuller's earth in the United States was 29,000 tons (£58,800) in 1910, and 36,600 tons (£76,000) in 1911; the mean value is less than £2 per ton at the place of production. Florida in 1911 contributed about 25,000 tons, produced by various companies. The United States imported 15,200 tons in 1910 and 16,400 tons (£28,800, *i. e.*, £1 12*s*. per ton) in 1911.

FIG. 285.

Such earths were first used in the United States in 1891, but solely for mineral oils, whilst for vegetable and animal oils English Fuller's earth was employed. Only after 1910 was it found that the Fuller's earth of Arkansas is even better than that from England for edible oils. In Georgia there are abundant deposits of this earth, and others have been found in other American States.

English Fuller's earth (from Kent, Dorset, and Surrey) is ground at the mines, subjected to levigation to free it from sand and stones, and then dried. The American product is, however, often pure, and it suffices to dry, grind and sieve it to the desired degree of fineness (sieve No. 100; the finer it is, the better it decolorises); the drying is carried out in revolving cylinders like those used for heating cement (*q. v.*). American Fuller's earth (but not the English) gives to the oil a peculiar taste and smell, which are removed by passing dry steam into the oil heated at 100°. Acid oils are decolorised only after washing with dilute alkali. Earth which has been used to decolorise oils may be used again after treatment with a mixture of benzene, alcohol, and acids. Certain of these earths are employed to discharge the colour of various highly coloured cloths. The earths are acid in character and readily absorb basic colouring matters (malachite green, methylene blue, fuchsine, etc.); they also decolorise aqueous solutions of such colouring matters, forming true insoluble pigments. Acid colours are not absorbed.

[2] *High temperatures are measured* with electric pyrometers (*see* Rhodium) or more commonly by means of the so-called Seger cones, which are small, elongated, triangular pyramids, 6 cm. high and with a base of 2 cm., formed of aluminium silicate and more or less alkali and lime. They are stamped with conventional numbers with which definite temperatures correspond (*see* Table on next page). If they are introduced into a furnace of which the temperature is to

coloured on fusion and should not effervesce with acids (absence of carbonates).[1] Clays for castings, fireclay, pumice stone, etc., have all a basis of aluminium silicate, but also contain free quartzose silica and other impurities.[2]

---

be measured, then by observing which cone commences to be vitrified and then softened and bent until its point touches the floor or the tile on which it is placed, the temperature is determined (*see* Fig. 285).

Number of cone	Melts at about	Number of cone	Melts at about	Number of cone	Melts at about	Number of cone	Melts at about
022	590°	08	990°	7	1270°	26	1650°
021	620°	07	1010°	8	1290°	27	1670°
020	650°	06	1030°	9	1310°	28	1690°
019	680°	05	1050°	10	1330°	29	1710°
018	710°	04	1070°	11	1350°	30	1730°
017	740°	03	1090°	12	1370°	31	1750°
016	770°	02	1110°	13	1390°	32	1770°
015	800°	01	1130°	14	1410°	33	1790°
014	830°	1	1150°	15	1430°	34	1810°
013	860°	2	1170°	16	1450°	35	1830°
012	890°	3	1190°	17	1470°	36	1850°
011	920°	4	1210°	18	1490°	37	1870°
010	950°	5	1230°	19	1510°	38	1890°
09	970°	6	1250°	20	1530°	39	1910°

[1] The iron is eliminated from kaolin by washing either with dilute sulphuric acid or with hydrochloric acid, but the operation is inconvenient and costly. According to Ger. Pat. 245,164, 1910, it is easier and cheaper to treat 100 kilos of kaolin with 200 litres of water, 200 grms. of concentrated sulphuric acid, and 200 grms. of sodium hydrosulphite; after half an hour's stirring all the iron dissolves, the liquid being decanted off after standing, and the residue washed with water, etc.

[2] **Pumice stone** consists of a silicate of aluminium, soda and potash, and is a porous, light, shining grey volcanic stone, often of fibrous structure; its density is 2·3 to 2·6 and its hardness 6 to 7. It is not attacked by acids. In the powdered form it is mixed to a paste with sodium silicate, bricks of artificial pumice being thus obtained. It abounds in the Lipari Islands (Monte Pelato), where there are thirty quarries, the exports in 1912 being 27,944 tons: 8100 to Germany, 8260 to the United States, 3500 to England, 3064 to Belgium, 1820 to the Netherlands, 1000 to Italy, and 1000 to France. The output in Italy in 1908 was 15,000 tons (£24,000) and in 1913 14,937 tons (£16,120). Pumice stone occurs in abundance also at Santorino (Greece). It is used for cleaning metals, wood and marble, and, along with agglutinants, to make glass paper. It costs £10 to £12 per ton in lumps or £4 to £6 in powder.

Fireclay for the preparation of firebricks should have not only a definite chemical composition and a high melting-point, but also a dense and compact physical constitution. The composition of fireclay should be about 43 to 47 per cent. of SiO_2, 37 to 39 per cent. of Al_2O_3, 1 to 1·5 per cent. of Fe_2O_3, 0·2 to 0·8 per cent. of CaO, 0 to 0·4 per cent. of MgO, 0·4 to 0·7 per cent. of alkali, and 12 to 15 per cent. of loss in weight on ignition, but in order to render it more infusible this clay is mixed with other clay previously baked several times, for instance, with fireclay bricks which have been previously used and are then called *chamotte.* It is then coarsely ground and is used to thin down other fatter clays which have, however, the density and compactness of fireclay, and renders them less easily attacked by basic ashes in the furnace in which it is employed. Clay and chamotte are mixed by millstones or vertical stones; after the mass has been slightly moistened, it is then compressed into bricks in suitable moulds. The bricks are baked in furnaces at a temperature between Seger cones 10 and 20 (*see* preceding Note). To eliminate from clay the substances which lower its melting-point (anti-refractories) it is subjected to levigation after treatment with hot water in revolving drums; the resulting clay is more homogeneous and is collected at once in filter-presses and not by removal of the water by decantation. It is then again placed in the mills, the chamotte being added. The dry, powdered mass is freed from iron by passing it over electromagnets, and is then moulded dry (only 6 to 8 per cent. of water) in moulds under high hydraulic or mechanical pressure exerted simultaneously in opposite directions; this moulded material may be placed in the furnace without previous drying or heating. In the wet process it is mixed with 15 to 30 per cent of water; the drying is carried out in suitable galleries, and when the moisture is reduced to 6 to 8 per cent., a pressure of 500 to 800 kilos per sq. cm. is applied, the rest of the water being afterwards expelled.

Still more infusible materials (for example, *Dinas bricks*) are obtained by adding quartz or by starting from quartz sand which is mixed with 2 per cent. of gypsum and 1 per cent. of aluminium sulphate, as the particles of quartz then become cemented at the plastic point during baking. A mass containing 92 to 94 per cent. of SiO_2 and 4·5 to 5·5 per cent. of Al_2O_3 is thus obtained; these bricks are used for building the arches of glass kilns or of Martin steel furnaces, where the temperature is 1750° to 1800°, but are sensitive to sudden temperature fluctuations and slightly increase in volume on baking. These refractory quartz bricks (at least 90 per cent. SiO_2, a little clay and not more than 2 per cent. of CaO in the form of milk of lime, as an agglu-

Sand as an impurity influences the plasticity unfavourably, whilst iron and lime alter it very little. Magnesia, and also lime to a less extent, diminish the refractory properties. Good commercial kaolin contains 43·5 to 46 per cent. of SiO_2, 39 to 39·8 per cent. of Al_2O_3, 13 to 13·9 per cent. of water, less than 5 per cent. of quartzose silica, and less than 2 per cent. of felspar or mica.[1] Ceramic materials may be divided into two groups: Compact

---

tinant) do not contract, but rather expand on baking, this being partially remedied by damping the fire and spraying with water at a red heat; the bricks should be cooled very slowly. Good Dinas bricks (the best are the German stella bricks, prepared from amorphous tertiary quartzite containing 98 per cent. of SiO_2 from the Westerwald basin), are able to withstand, in the Martin steel furnace, as many as 600 to 800 castings, whereas ordinary common varieties last only for 250. The only quartzites suitable for making Dinas bricks are those showing yellow spots, which, according to S. Franchi (1917), are due to the presence of titanium dioxide (rutile); as a rule they contain less than 1 per cent. of titanium.

Magnesia firebricks are obtained in the electric furnace, in which the ferric oxide is evaporated (at 1800° to 2000°); there remains a hard compact mass of MgO of saccharoid appearance, polymerisation occurring at 1900° to 2200°.

Bauxite firebricks (the white are less readily fusible than the red ones rich in iron) are prepared from bauxite previously baked to obviate marked contraction and deformation; to this end the finely ground bauxite is made into a paste with organic agglutinants (glue, gum, etc.), and compressed into bricks under a high pressure. The bricks thus formed are subjected to intense baking, then ground finely, and mixed well with plastic clay, and made again into bricks under a high pressure and baked in the furnace. Bauxite firebricks last 6 to 7 times as long as ordinary firebricks and are highly resistant to the action of chemical agents.

The *infusibility* of firebricks increases with *Bischoff's coefficient*: $\frac{Al_2O_3 + SiO_2}{\text{bases}}$; by the term "bases" the sum of the oxides of Fe, Ca, Mg, K, and Na is here understood, and this should not exceed 3 per cent. of the total, but for inferior materials is sometimes as much as 7 per cent. Increase of Al_2O_3 increases the refractory properties of the brick and its resistance to chemical agents. The melting-point is lowered to the same degree whatever the base introduced if equimolecular proportions are taken, so that 1 mol. of MgO produces the same depression as 1 mol. of CaO; thus, for equal weights of MgO and CaO it is lowered more by the MgO, because this has a lower molecular weight. In very basic minerals, such as *talc* ($3MgO,4SiO_2$), the alumina, Al_2O_3, lowers the melting-point. Thus, on mixing talc, which melts with Seger cone 31, and kaolin ($Al_2O_3 + 2SiO_2$), which melts with cone 36, a product is obtained which melts with cone 11. The addition of silica to clay lowers the melting-point (acid silicates), and the maximum depression is obtained with a proportion of 1 mol. of clay and 17 mols. of SiO_2, and for equal contents of SiO_2 that mixture melts at a lower temperature which contains the SiO_2 in a more finely divided state. Materials of coarse grain resist temperature fluctuations better than those of fine grain.

The *temperatures of fusion* of firebricks are as follows: ordinary, 1555° to 1725°; bauxite bricks, 1565° to 1785°; Dinas, 1700° to 1705°; chromium, 2050°; magnesia, 2165°; kaolin, 1735° to 1740°; bauxite, 1820°; chromite, 2080°; pure alumina, 2010°; quartz or pure silica, 1750°; silicon carbide, 2700° (partly decomposes before this); uranium carbide, 2425°; vanadium carbide, 2750°; CaO, 1995°; Al_2O_3, 2020°; Cr_2O_3, 2059°; ZrO_2, 2500°.

In 1907 Italy imported 8450 tons of fireclay bricks and in 1908 5500 tons, of the value of £112,000.

In 1909 Germany exported 170,000 tons of refractory materials and imported 35,000 tons.

Foundry clay. The best qualities contain 80 to 90 per cent. of SiO_2, almost entirely in the form of siliceous quartz, and 15 to 18 per cent. of alumina with traces only of lime and magnesia. This product comes from France (Boulogne) and costs 2*s.* 5*d.* to 3*s.* 2*d.* per ton on the spot; at Milan it costs £1 to £1 4*s.* per ton, including freight.

The clays which are found in Italy are of poor quality, and cost 4*s.* 10*d.* to 9*s.* 8*d.* at Milan. Near Pavia and Cavamanara there are poor qualities of foundry clays which cost 4*s.* 10*d.* per ton at Milan.

[1] In Italy good kaolin is rare; it is found near Schio (Tretto), near Novara (at Borgomanero), in Valtellina (Monte Zebrio), Tolfa (Rome), Lucca, Catanzaro (Sardinia) and Sicily. Important deposits are found in France (near Limoges) and England (Cornwall). It abounds in Germany and Hungary, and ancient deposits are found in China and Japan. English kaolin is whiter but less plastic than French and costs less.

The world's consumption of kaolin was 680,000 tons in 1906 and 900,000 in 1911.

For Italy the statistics are as follows (tons):

	1907	1910	1911	1912	1913	1914	1915	1916	1917
Production .	8,350	5,400	5,930	7,650	11,920	14,680	13,920	25,106	—
Importation .	16,534	31,863	28,301	25,577	25,972	28,240	15,821	17,986	14,322

France imported 61,256 tons of kaolin in 1913, 45,689 in 1914, and 14,000 in 1915. England produced 900,000 tons in 1911.

The price of the porcelain qualities is 16*s.* to 24*s.* per ton, the best quality costing £1 12*s.*

The output of felspar in the United States was 92,000 tons (£116,000) in 1911 and 86,000 in 1912. The price of the crude product was 12*s.* 9*d.* per ton, and when ground £1 8*s.* It is used especially in the ceramic industry to prepare glazed bricks and electrical fittings, also as an adhesive in making grindstones, and in the manufacture of glass, tiles, etc.

materials which are semi-vitrified and semi-fused, translucent, very hard, impermeable to water and do not adhere to the tongue, and comprise true *glazed porcelain* (soft and hard), *statuary porcelain* or unglazed biscuit-ware, and *stoneware*, glazed or unglazed, semi-vitrified, but not semi-fused, and non-adherent to the tongue.[1]

---

[1] **Stoneware** has acquired great importance to-day for the manufacture of drain-pipes and conduits for impure liquids of acid or slight alkaline reaction. It is also very largely used for the most varied chemical plant (receivers, rings for towers, cocks, heating stoves, coils, various condensing and distilling plant, etc.), and generally has a semi-vitrified surface and brownish grey or yellow-brown colour, which varies according to the quantity of iron silicates contained in the clay from which it is formed. This should contain little or no calcium carbonate, but sufficient quantities of fluxes (alkali silicates, felspar, and quartz) to allow the paste to be exposed directly to baking, because although the fusion point of these fluxes is very high (up to Seger cone 26) they soften and thicken at lower temperatures (up to cone 4).

The colour varies also with the reducing or oxidising character of the flame in the kiln, being grey when this has a reducing action and yellow when it has an oxidising action, and the colour is more intense with rise of temperature. The best qualities of clay for stoneware are found in Germany along the Rhine and the Elbe and in Nassau; much is also found in Bohemia, and it is not lacking in various parts of Italy, but is of inferior quality. The composition varies considerably, but may be corrected by levigation or by addition of fatter or leaner clay and also by addition of chamotte powder (*see* preceding Note); the chemical composition generally varies between the following limits: SiO_2, 60 to 70 per cent.; Al_2O_3, 20 to 25 per cent.; Fe_2O_3, 0·8 to 1·8 per cent.; $CaO + MgO$, 0·5 to 1·2 per cent.; $K_2O + Na_2O$, 1·5 to 3·5 per cent.; H_2O, 4 to 9 per cent. (together with organic matter). The best clays approximate to 70 per cent. of SiO_2 and 22 to 23 per cent. of Al_2O_3. The materials are worked up in mixers, mills and presses and allowed to mature, and the ware is baked in the same manner as with porcelain, and in order to obtain the surface glaze sodium chloride is thrown into the furnace or into the gases during burning towards the end of the baking when the furnace has a temperature of 7 to 8 Seger cone. The sodium chloride is decomposed by the steam in the gases into HCl and NaOH. The latter forms a mist which covers the surface of the stoneware objects and vitrifies it, forming an alkaline aluminium silicate. The vitrification may be obtained also by dipping the unbaked ware into a glaze consisting of a suspension of brick clay and a little limestone, or of a pulverised mixture consisting of 17 parts of felspar, 7 parts of marble, 5 parts of kaolin, and 11 parts of quartz. On baking at 1300° to 1350° the articles should undergo practically no alteration of shape if the raw materials are homogeneous and of good quality. The finished and baked ware is allowed to cool slowly in the furnace, care being taken to avoid the least draught which would cause cracking. Good earthenware vessels should show no efflorescence on the surface when filled with water, even after 20 or 30 days. When the fracture of a piece of earthenware is moistened with a drop of ink, this should not spread: sign of fine grain and good baking. The baking occupies altogether about fifty hours and the consumption of brown coal is about 100 kilos per cu. metre capacity of the furnace (for small furnaces of 25 cu. metres it rises to 130 kilos and for those of 100 cu. metres it falls to 80 to 85 kilos) and 2 to 3 kilos of salt are used per cu. metre.

The linear *contraction* during baking is 10 to 12 per cent. for earthenware, and more for porcelain, and it increases with the fineness of grinding (the mass becoming more compact). Material ground for two hours gives a residue of 8·28 per cent. on a sieve with 9200 meshes (100 grms. of the material is mixed with 25 grms. of water). When ground for four hours it gives a residue of 2·16 per cent. and a contraction of 10 per cent.; after six hours the residue is 0·5 per cent. and the contraction 11·11 per cent., and after eight hours the residue is 0·16 per cent. and the contraction 12·22 per cent.

Good earthenware is obtained with a composition of 45 per cent. of alumina (clay), 43 per cent. of quartz, and 12 per cent. of felspar, the ground mass mixed with water being passed through a sieve with 5400 meshes per sq. cm. The formed articles, after drying in the air and before the final baking, should be heated for a long time with a low fire to above 1000°, since the water of hydration of the clay is evolved up to 1050° and the water vapour surrounds the organic particles of the mass and the carbonaceous matter from the gases absorbed by the porous mass, thus preventing their combustion by the oxygen of the hot air. When the evolution of steam ceases completely and the heat is suspended for a couple of hours, the air is able to penetrate the pores of the mass and to burn the organic and carbonaceous particles deposited during the smoking; only after this phase is the final heating effected to the temperature of incipient vitrification, namely, 1250° to 1280° (earthenware fuses at about 1600°). Long flaming gas coal is used in these furnaces. In general the contraction is complete before the water is entirely expelled. Suitable regulation of the flue draught gives in the furnace either an oxidising atmosphere (which yields yellow or reddish-brown earthenware if the mass contains less than 10 per cent. of Fe_2O_3), or a reducing atmosphere (which gives a grey earthenware or one with blue reflection like Doulton ware), or a neutral atmosphere (yielding intermediate types). During salting the atmosphere is reducing, this being followed by an oxidising atmosphere with a low draught.

Exposure to frost and to summer heat and the concurrent fermentation increase the colloidal substances which render the clay more plastic. In general the presence of hydrogen ions (acid compounds) accelerates the coagulation of the colloids and the increase of plasticity, whilst the presence of OH ions (basic compounds) produces the opposite effect. The addition of finely powdered quartz to the clay or kaolin diminishes the contraction and deformation of the articles during the drying and baking.

Porous Ceramic Materials which are not vitrified have an earthy fracture, absorb water, adhere to the tongue, and include (1) *majolica*, with an opaque superficial glaze and dark internal body; (2) *terraglia* (*fine faience*) with a white, porous internal body and transparent glaze; (3) *coarse earthenware*, more or less coloured with an opaque glaze of various colours; (4) *bricks* or constructive materials of baked clay, unglazed and refractory; (5) *plaques, tiles, and terra-cotta*, ordinarily coloured red.

PORCELAIN is manufactured by working up kaolin to a paste with felspar and well-powdered quartz in definite proportions, so that the porcelain may become less porous, contract less and take a better glaze. At high temperatures in suitable furnaces the felspar and quartz melt, and are incorporated by the kaolin, forming a very hard compact mass. The kaolin is obtained in a very fine powder by means of systematic levigation; the felspar and the quartz are rendered more friable by first heating them in a furnace and then powdering them in ball mills (p. 652), or by submitting the powder to regular levigation with water. The pulverised material is freed from iron particles from the machinery by passing it over magnets during levigation. The paste is prepared in various proportions in different works, for example, 45 to 65 parts of kaolin, 10 to 30 parts of quartz, and 5 to 20 parts of felspar, and these ingredients are intimately mixed in large vats by stirring with water; the homogeneous paste is collected in filter-presses in a compact form, and is then allowed to stand for some time in a moist spot where it undergoes a kind of putrefaction (maturing) which somewhat increases its plasticity by the formation of colloidal substances (*see* p. 107); during this maturing process there is a slow evolution of CO_2, NH_3, and H_2S. After this it is repeatedly kneaded and rekneaded until it is ready for modelling, which is carried out with various instruments and perfected machinery which allow the work to be performed rapidly and exactly—wheels, moulds, etc. For hard porcelain the fundamental mixture consists of 50 per cent. of clay or kaolin, 25 per cent. of felspar, and 25 per cent. of quartz. Increase in the proportion of quartz lowers the fusion temperature and addition of alumina previously heated to redness or fused in the electric furnace enhances the resistance to heat; thus, 30 per cent. of kaolin, 25 per cent. of felspar, and 45 per cent. of alumina gives a mass melting at 1830° and with a total contraction of 18 per cent.

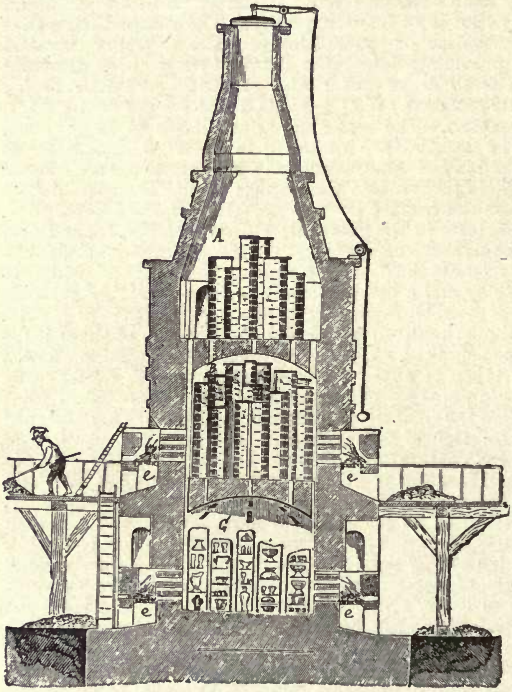


FIG. 286.

Equimolecular proportions of CaO, SrO and BaO, added to porcelain or kaolin, lower the fusion temperature by amounts which are the greater the lower the molecular weight. Addition of magnesia to porcelain renders the latter more resistant to sudden cooling.

Zöllner, Roesner, and Woods have found that porcelain baked at a high temperature shows under the microscope a crystalline substance (sillimenite), which is not formed at lower baking temperatures, and that the electrical insulating power of porcelain is related to this substance. The coefficient of expansion of porcelain is 0·000005357.

Addition of a little calcium or aluminium sulphate to the fluid kaolin or clay paste for porcelain increases the tenacity, but excess of these sulphates renders the mass fluid again, so that clays rich in calcium or magnesium sulphate are unsuitable for porcelain.

The modelled objects are allowed to dry slowly in the air, and then undergo a first baking in suitable furnaces so that they may acquire a certain degree of hardness, after which they are more readily handled and glazed. A type of furnace commonly used is that illustrated in section in Fig. 286, and contains three floors communicating with one another by flues left open in the vaults. In the upper floor, *A*, the first baking of the porcelain is carried out by setting it down cautiously in boxes of refractory clay covered and placed on one another in stacks in such a way that the gases from the hearth, *e*, do not stain the articles. In this chamber the temperature reaches 900°, and this suffices to remove all the chemically combined water from the porcelain. When the objects have cooled they are removed from the chamber and are glazed in a bath containing an aqueous suspension of a powdered mixture of the glaze or enamel, composed of kaolin or felspar, sand, and marble.

The components of the glaze melt at the temperature at which the porcelain is baked, forming an enamel which becomes transparent and hard in the cold.[1]

The objects are then placed in their respective clay boxes and arranged in stacks in the two other chambers of the furnace, *B* and *C*. It is necessary carefully to regulate the temperature, and also still more the nature of the gas used for heating the porcelain. The furnaces are heated with wood or coal by means of five hearths (*e*) on each floor. To-day Siemens' regenerative furnaces are often used (p. 634) and allow an almost white heat to be attained. Before reaching this temperature, however, the gases should be of a reducing character in order to destroy the yellowish colour of the porcelain due to iron oxide, Fe_2O_3, but at certain periods the gas should be slightly oxidising in character in order to burn the carbon deposited on the material. The temperatures are nowadays determined exactly by means of electric pyrometers which register the temperature of the kiln at any moment, even at a distance. The kilns are to-day constructed of refractory material and work continuously, and when one chamber is heating the other is cooling, whilst the third is discharged and recharged. The cooled material is removed and checked in order to separate defective pieces from those which are satisfactory.

Egg-shell porcelain is much used in France and in England. It does not contain kaolin, but is formed of a vitreous mass consisting of an alkaline earth silicate, which is covered with a lead glaze of the same composition as flint glass. It melts easily and has the appearance of a milky glass, translucent and devitrified. It is obtained by mixing 60 parts of sand, 23 of potassium nitrate, 7 of sodium chloride, 3·5 of soda, 3·5 of gypsum, and 3·5 of burnt alum. This mixture is heated (*fritted*), and the product is pulverised and mixed with 17 per cent. of chalk and 8 per cent. of *marl* (aluminium silicate mixed with calcium carbonate). Egg-shell porcelain, glazed or unglazed, is used for many ornamental objects and is better suited than hard porcelain for coloration in very varied tints.

Bricks and **Tiles** are to-day manufactured with the help of highly perfected machinery. Comparatively impure and coloured clay is more or less suitable for the manufacture of bricks. Chalky clay, which contains much calcium carbonate and gypsum, forms bricks which change their volume greatly in the kiln, as they lose CO_2 and H_2O, but then swell up and crumble on exposure to the air. Ceramic clay is sometimes purified nowadays by the electro-osmotic method, since, when a current is passed through a suspension of clay in water, the particles of clay accumulate at the anode; with a consumption of 250 kilowatt-hours, 10,000 kilos of clay with 15 to 30 per cent. of moisture can be separated. The composition of clay for bricks should be within the following limits: SiO_2, 43 to 61 per cent.; Al_2O_3, 26 to 39 per cent.; MgO, 0 to 1·5 per cent.; CaO, 0 to 1 per cent.; Fe_2O_3, 0 to 2·5

---

[1] Enamels for metallic objects (for cooking and for chemical purposes) are to-day prepared from mixtures free from lead and containing a little tin oxide. On the tile or iron object heated in a muffle a fusible enamel is first placed, for example, 17 parts of quartz, 30 of felspar, 46 of borax, 2 of soda, 3 of sodium fluosilicate, 2 of saltpetre, 0·18 of cobalt oxide, 0·42 of nickel oxide, and 0·03 of copper oxide; the whole is melted and, after cooling, is ground with the addition of 7 per cent. of clay or kaolin. On to this fusible enamel an opaque, white shining enamel is then superposed, consisting of the following mixture: quartz 10·5, felspar 37·5, borax 18, cryolite 12, and nitre 0·7 parts. This mixture is melted and after cooling is ground with the addition of 7 per cent. of kaolin and 8 per cent. of tin oxide. At one time tin oxide was used to the extent of 40 per cent., in order to obtain white, opaque enamels, but it is now partially replaced by cryolite, and this has recently been replaced by sodium fluosilicate, which is still cheaper.

Stull and Radcliff have shown that addition of boric acid to basic enamels (for porcelain) increases the readiness with which the enamel surface cracks, whilst such addition to markedly acid enamels obviates this inconvenience. Cracking occurs when the coefficient of expansion of the enamel is greater than that of the porcelain substrate, and in general boric acid lowers this coefficient; PbO raises it more than CaO. Enamels containing cupric oxide exhibit great tendency to crack.

per cent.; $Na_2O + K_2O$, 0 to 5 per cent.; SO_3 (as sulphates), 0 to 2 per cent.; loss on ignition (CO_2, etc.), 7·35 to 18 per cent. Fragments of small siliceous pebbles are harmful, as they swell during baking and then burst the bricks. Pyrites is also harmful, because the iron sulphide which is formed in the kiln becomes oxidised to the soluble sulphate in the air, and the bricks become friable. One cubic metre of clay weighs 1·5 ton. After the preparation and maturing of the clay it is worked to a paste and the mixture shaped into bricks, this operation being now carried out by highly perfected machinery which we cannot describe here. Mention may, however, be made of the first such machine, devised by Schlickeysen in 1855, with which the homogenisation of the mixture and the simultaneous formation of the bricks were carried out continuously by means of large screws revolving in the pasty mixture; machines of this type are still largely used. The unbaked bricks, after drying in the air or in hot gases, are baked in suitable kilns, either open or closed, which at one time worked intermittently, but are now generally worked continuously. Of the latter the annular kiln of Hoffmann (1858) is the most generally used and has undergone many improvements. In Fig. 287 we see it in section, and at the bottom to the right is a transverse section of the chambers, 8 to 13, or *B*, and to the left a longitudinal section of the kiln which has fourteen chambers, 1 to 14, forming a long single passage in which the walls dividing one chamber from the other are removed provisionally when one or the other is to be emptied or filled with the material. Each chamber has a door (t_1 to t_{14}), and at the diagonally opposite corner an outlet flue (r_1 to r_{14}) for the gases, with an opening adjustable by the valve, *V*, leading into a common flue, *R*, which carries the products of combustion to the chimney, *E*. Of the 14 chambers, 12 are charged with bricks (each of them being capable of holding more than 10,000), whilst one chamber, for example, No. 1, stands empty, and the last one, for example, No. 14, is being charged. If an iron (or plaster nowadays) dividing wall is introduced between chambers 13 and 14, and all the doors, t_2 to t_{14}, and all the flues, r_{14}, r_1 . . . r_{12}, are shut down, the door, t_1, and the flue, r_{13}, being left open, then the chimney, *E*, will draw in a current of gas and air, which, entering through the door t_1, will pass into the chamber A_1, then into A_3 . . . up to chamber 12, and will thence escape along the flue r_{13} and reach the chimney.

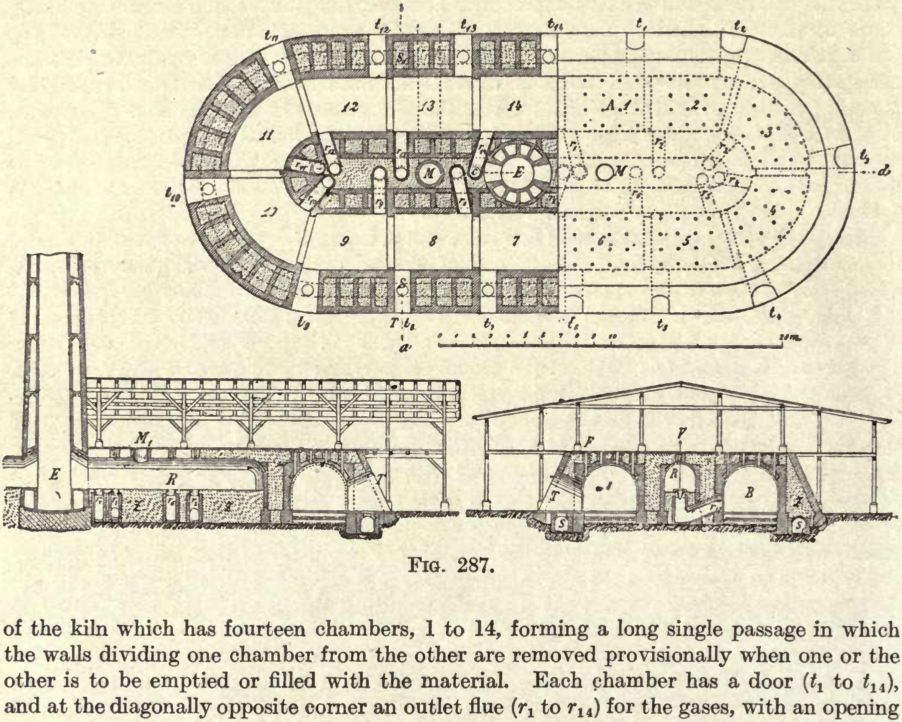


FIG. 287.

The current of gas cannot travel in the opposite direction, because the wall between 13 and 14 is closed, whilst all the other chambers are without dividing walls.

The heat is produced from wood or coal which is introduced into several vertical channels, *F*, in the vault of each chamber, and the gas and the air, entering cold at *t*, cool the already baked material and enter hot into the first chamber, and thus in turn the gases get continually hotter, so that near chamber 8 they acquire a maximum temperature which suffices, together with the fuel, to bake the bricks in the succeeding furnaces. Work is continuous, because with a movable door one may successively isolate one chamber for discharging and another for charging. The Hoffmann kiln has undergone various small modifications, but the fundamental principle on which it is based is always the same. The complicated flues have been replaced by a simple tube for carrying off the gases.

The saving of fuel with this kiln was marked, since not only are the bricks to be baked subjected to their preliminary heating by the gases, but the heat of the baked bricks is utilised by cooling them with air and using the latter afterwards for burning the coal. At the present day heating by means of gas producers is employed (*see* p. 634).

For several years this same furnace has also been applied in the hydraulic cement industry, for which very high temperatures, higher even than those necessary for the preparation of bricks (*see below*), are required.

The more or less red colour of bricks is due to the greater or smaller amount of iron oxide in the clay. The tile industry has undergone notable improvements of late years, and Upper Italy has already started an important export trade which is certain of a successful future.

STATISTICS. Considerable quantities of kaolin are also employed as a weighting material in the manufacture of paper. In Italy there are deposits of kaolin in the provinces of Saluzzo, Novara, Vincenza (at Tretto near Schio), Civitavecchia (at Tolfa), Pisa, Bologna, and in Sicily. These kaolins are well adapted for the preparation of white majolica, and 15,500 tons were produced in Italy in 1902, whilst that required for hard porcelain was imported from England. In 1902 about 14,000 tons of the value of £2200, and in succeeding years the quantities shown in the Table on p. 740 were imported; four-fifths of this came from England, which supplies the best qualities. Germany imported 248,736 tons of kaolin in 1909 and exported 27,000 tons.

The ceramic industry is continuously progressing in Italy, and whilst in 1885 earthenware and porcelain to the value of more than £120,000 were imported, in 1901 the imports diminished to less than £80,000, over and above an internal production of more than £600,000, of which £320,000 is provided by the works of Richard Ginori at Florence and Milan alone, which is the most important in the world, especially for artistic ware and for ceramic paintings. In 1903 Italy produced 23,000 tons of refractory materials and stoneware (25,500 tons in 1908, of the value of £68,000), 36,000 tons of majolica and common earthenware (in 1908 more than £540,000, and 2280 tons of majolica and artistic ceramic ware for £67,240), and 4000 tons of porcelain (the exports of porcelain in 1908 were worth £143,520). In 1904 1400 tons were imported at £80 per ton, and 2400 tons were exported, of the value of £15,200.

In succeeding years the production, importation, and exportation of the ceramic industry in Italy were as follows (tons):

		1910	1911	1912	1913	1914	1915	1916	1917
Bricks, tiles, etc. .	prod.	6,584,051	6,584,051	6,889,151	—	—	—	—	—
	imp.	1,911	1,015	976	317	404	2,070	3,940	17,450
	exp.	99,196	97,638	105,574	119,449	68,285	3,446	1,925	3,653
Refractory materials and ordinary earthenware	prod.	23,880	23,880	23,880	—	—	—	—	—
	imp.	64,350	57,950	55,905	1,119	37,680	18,278	49,102	32,003
	exp.	813	1,611	2,862	1,702	2,016	4,891	1,786	2,731
Terra cotta (pots, piping, vases, etc.)	prod.	80,091	80,091	88,721	—	—	—	—	—
	imp.	4,511	5,684	5,358	4,593	3,755	1,880	5,586	4,067
	exp.	6,476	13,108	15,663	15,683	13,314	16,701	11,035	1,900
Ordinary majolica and pottery	prod.	35,343	35,343	36,703	—	—	—	—	—
	imp.	2,665	3,350	2,808	3,094	2,018	645	157	135
	exp.	472	445	486	1,312	1,556	2,168	3,185	2,195
Artistic majolica and pottery	prod.	2,281	2,281	3,231	—	—	—	—	—
	imp.	885	834	790	—	—	—	—	—
	exp.	1,083	846	370	—	—	—	—	—
Fire porcelain and earthenware	prod.	4,011	4,011	4,011	—	—	—	—	—
	imp.	3,940	4,040	4,329	4,705	3,417	1,596	482	634
	exp.	153	157	245	360	237	349	433	163

ARTIFICIAL BRICKS AND STONES (Arenolite or siliceous-argillaceous-calcareous stone). This industry has now acquired great importance in various countries after twenty years of experiment and persistent work,[1] and it will certainly not be long before it also develops in Italy, although the two works which were started closed before 1910 owing to imperfect machinery, excessive freight on the sand, and commercial adversity. A works erected near Tripoli for using the sand of the desert does not seem to have given the results expected, possibly owing to incomplete study of the raw material, since the author has found in certain regions and at certain depths sand of the exact composition to yield, without any addition, arenolite bricks. Of the numerous patents which now exist, those based on the Girard-Meurer process possess special industrial importance.

When intimately mixed and compressed, lime and silica combine rapidly under the simple action of high-pressure steam, forming a compact mass of calcium silicate which is more or less hydrated.

Girard improved the materials by adding a very small quantity of raw clay, which gives a harder stone in a shorter time. The artificial stones are thus siliceous-argillaceous-calcareous agglomerates, forming a hardened hydraulic cement under the action of high-pressure steam.

Powdered quicklime is used in the proportion of 1 part of lime to about 10 parts of hot, dry, siliceous sand; a little powdered, raw clay (not calcined; to the extent of about 3 per cent. of the lime) is then added, and after moistening with hot water (30 per cent. of the weight of the lime in order just to obtain the hydroxide) the whole is well mixed and a further 7 per cent. of the total weight of hot water is added in order to enable bricks of compact form to be obtained more easily in the presses. On removal from the press, the bricks are arranged on cars and introduced into suitable furnaces in which they are exposed to high-pressure steam.

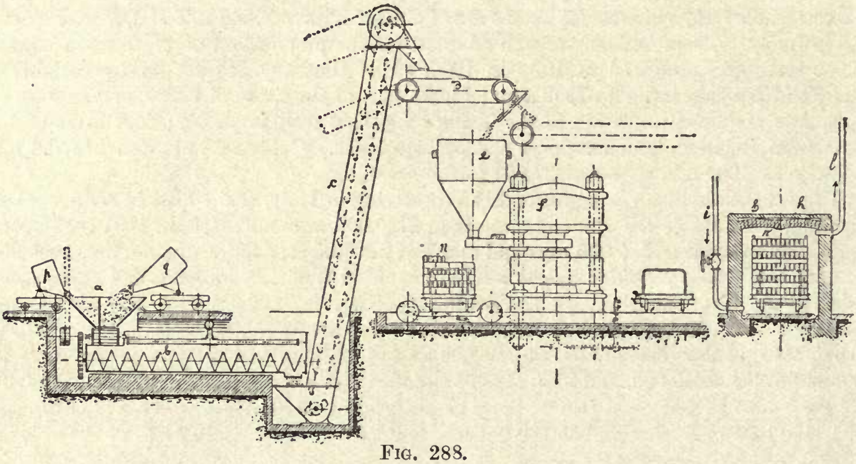


FIG. 288.

In order that the final result should be good, it is indispensable that the quicklime should be completely slaked and that the physical nature of the sand (fineness and the round or jagged form of its particles, etc.) should be taken into account. In the case of fine quartzose sand, a comparatively small quantity of lime is needed. With fine slaked lime (separated by means of a fan) bricks more resistant to pressure are obtained.

---

[1] Dr. Zernikow in 1877 was the first to mix siliceous sand with freshly slaked lime, and he exposed the mixture to the action of steam under pressure (5 to 8 atmospheres) for 6 to 12 hours. After this the mass was moulded into shapes and compressed. Stone of the highest qualities, which is more fully described above, thus resulted. In 1880 Michaelis showed that this was due to the action of steam at high pressure on silica. Others, on the other hand, first pressed the bricks and then exposed them to the action of high-pressure steam for 3 to 6 days (Gressy, Neffgen, Meurer, Becker, and Klee, 1882 to 1898). Pfeiffer in 1894 and Olschewsky in 1898 endeavoured to produce hardening of the stone by utilising the heat evolved in the slaking of the lime, but did not meet with much success. The manufacture of artificial stone only became practical in 1899, when every uncertainty was removed through the improvements of Meurer and the modification then introduced by Girard, that is, the addition of clay as a new component. Many works in almost every country now use the Girard-Meurer process. In Germany there are more than 200 works, and of these the Guttmann works near Berlin alone produce more than 200,000,000 bricks per annum.

An excess of lime must be avoided, because if this remains unaltered, it absorbs CO_2 from the air and detracts from the quality of the bricks. When these have been moulded, they should not remain exposed to the air, but should immediately be treated with steam under pressure.

The necessary arrangements are shown diagrammatically in Fig. 288. The hot material is carried to the hopper, *a*, in cars, *p* and *q*; from these it passes into the mixer, *b*, and thence along the elevator, *c*, and an endless band, *d*, to the vessel, *e*, from which the homogeneous mixture passes into moulds in order to be strongly compressed in the press, *f*. The bricks thus compressed are loaded on to cars, *n*, and passed into the furnaces, *h*, which now consist of horizontal iron autoclaves up to 20 metres in length and 2 metres in diameter, into which compressed steam at a pressure of 8 to 10 atmospheres is introduced through the pipe, *i*. After 10 hours the reaction is complete and the bricks are ready for immediate use (they are placed in the furnace in the morning, the steam is let off in the evening, and they are removed on the following morning). For making 9000 bricks, 2350 kilos of steam are required to bring them to 170°, a further 930 kilos for heat lost by radiation, and 920 kilos to heat the condensed water (if not discharged): total 4200 kilos of steam, or 460 kilos per 1000 bricks. In order to increase the compactness of the surface of these stones, they are exposed to the action of hydrofluoric acid vapours, or are immersed in a solution of HF, and an extremely hard surface layer of calcium fluoride is thus formed, which resists the action of moisture, carbon dioxide, etc.[1]

The advantages of these artificial stones consist in their great regularity of shape, and in their strength, pressures of 400 kilos and more per square centimetre being withstood; they may also be employed for work under water; they are bad conductors of heat, very resistant to fire and as hard as cement, and may be painted or varnished directly and used immediately after manufacture; they absorb less water than ordinary bricks and dry rather more rapidly. Light artificial stones, either compact or perforated, are now produced with infusorial earth (kieselguhr).

The installation of a works for manufacturing such stone costs less than that of a brick-kiln and requires less space and less manual labour. The price of 100 bricks of the ordinary size (6 × 13 × 26 cm.) varies from 9*s.* 7*d.* to 12*s.* 10*d.*[2] The works in Berlin and neighbourhood produced 400,000,000 arenolite bricks annually before the Europeon War, and the total production in Germany amounted to 1000 millions.

HYDRAULIC MORTAR AND CEMENT

In almost all modern brickwork construction the employment of hydraulic mortar and cement is continually acquiring greater importance, not only for special work under water, but partially for replacing ordinary mortar. In the hardening of mortar (p. 617)

---

[1] In the preparation of stone by Michaelis' process, that is, by treatment with compressed steam, it has been observed that the amount of silica which combines with the lime to form calcium hydrosilicate increases with the pressure, and that at 10 atmospheres twice as much is combined as at 5 atmospheres. When fine sand is used, twice as much combined silica (7 to 8 per cent.) is obtained as when coarse sand is used (3 to 4 per cent.). In any case, however, only half the sand employed takes part in the reaction, but the amount which reacts may be increased slightly by compressing the bricks very strongly and employing fine sand. The hardness of the bricks is proportional to the quantities of combined silica and of uncombined lime, which in the course of time is transformed into carbonate. The use of superheated steam (200°) is not found to offer any advantage.

In the manufacture of artificial stone by Neffgen's process (the action of steam for 3 to 6 days without pressure at 99° to 99·5°) it has been observed that only 0·5 to 1 per cent. of the silica combines, whether little or much lime is used, or whether the sand is fine or coarse, or whether the steam acts for a longer or shorter time. The hardening this afterwards acquires is due to the formation of carbonate.

In either case the addition of clay does not appear to be of any advantage; in fact the addition of any other ingredient to the mixture of lime and silica is generally harmful or superfluous. The employment of lime produced from dolomitic materials, that is, materials rich in magnesia, does not matter, and only causes the cooling to be a little slower. Apart from pure fat limes, excellent results have also been obtained with medium hydraulic limes, for example, with one containing 12 per cent. of SiO_2, 1·85 of Fe_2O_3, 3·10 of Al_2O_3, 79·6 of CaO, 0·61 of MgO, and 3 of CO_2, water, etc.

[2] A works for the production of 50,000 artificial bricks per day would cost altogether about £12,000 and the daily expenditure would be as follows: 120 cubic metres of sand, £1 18*s.*; 10 tons of lime, £8; 2·8 tons of coal, £4 8*s.*; lubricants, replacements and various expenses, £1 12*s.*; 35 workpeople, £5 12*s.*; direction, administration, etc., £2; sinking fund and interest, £4 12*s.* Total per day = £28 2*s.*, so that per 1000 bricks the expenses are 11*s.*

we have seen that the silica of the sand does not take part except to an insignificant extent, and that the hardening depends almost exclusively on the action of CO_2 on lime with formation of hard calcium carbonate.

If, on the other hand, ordinary limestone containing a little clay and sand is heated to a temperature much below its melting-point, and the resulting lime then slaked with a little water, reducing it to powder, then on heating gently it hardens very quickly without any considerable increase in volume and forms *hydraulic cement.* The ratio between the clay (aluminium silicate) and the lime is called the *hydraulic index* (*see below*), and this in the case of *weakly hydraulic cements* (which give a residue of 10 to 15 per cent. with acids) formed from limestone with 5 to 8 per cent. of clay oscillates between 0·10 and 0·15; for *medium hydraulic cements* yielding 15 to 20 per cent of residue with acids and produced from limestone containing 8 to 15 per cent of clay, it varies from 0·15 to 0·30; for *common hydraulic cements* yielding a residue of 20 to 25 per cent. with acids and formed from limestone containing 15 to 19 per cent. of clay, the hydraulic index varies between 0·30 and 0·42, whilst for *strongly hydraulic cements*, yielding up to 30 per cent. of residue with acids, and obtained from limestone containing 19 to 21 per cent. of clay, the index varies from 0·40 to 0·45.

Above these limits we enter the category of true cements which harden more rapidly and strongly and are produced by heating argillaceous limestone, marls, etc., or from artificially prepared but chemically similar mixtures.

The **Hydraulic Cement of Palazzolo on the Oglio** is obtained from a deposit in a hill on the lake of Iseo. It is placed in kilns similar to lime-kilns and mixed with 12 to 14 per cent. of coal. Burnt lime more or less rich in free calcium oxide is formed at the bottom, mixed to form a conglomerate, that is, partially semi-molten into lumps. It is placed in heaps and then moistened after one or two days with a little water in order to slake the quicklime, remixed, then heated till it swells and falls to powder, and after 7 to 10 days passed into a sieve and then to mills (tube mills, *see below*, Cement). This hydraulic lime is sold at 12*s.* per ton.

In 1906 Italy produced 466,000 tons of hydraulic cement, of the value of £289,600, and in 1908 481,000 tons; the exports were 1230 tons.

We have already seen in connection with the production of arenolite that lime combines with silica with formation of calcium hydrosilicate if the mixture is heated in presence of steam under pressure, but if heated until they commence to fuse, certain rocks formed of aluminium silicate and calcium carbonate (calcareous marls) liberate CO_2 from the limestone, and a mixture (cement) of calcium silicate and aluminate remains, which is more or less basic and capable of being rapidly decomposed by water, forming a very hard mass:

$$6CaO + Al_2Si_2O_7 = 2Ca_2SiO_4 + Ca_2Al_2O_5.$$

With water this mixture reacts as follows:

$$(a) \quad Ca_2Al_2O_5 + 5H_2O = 2Ca(OH)_2 + Al_2(OH)_6$$
$$(b) \quad Ca_2SiO_4 + 2H_2O = CaH_2SiO_4 + Ca(OH)_2.$$

If the hardening of cement takes place in the air, the calcium hydroxide formed combines with the CO_2 of the air and forms calcium carbonate. Cements are partially attacked by mineral acids, least by sulphuric acid (*see below*, Theory of the Setting of Cement).

NATURAL CEMENTS. Even in ancient times mortars for use under water were known, and the Romans used the volcanic material of Pozzuoli and other places (the neighbourhood of Viterbo, etc), the *terra di Santorino* (a Greek island), and the *trass* which abounds in the Rhine Provinces.[1] After the time of the Romans these natural hydraulic cements were no longer used for many centuries, and it was only in 1841 that Weiler showed

---

[1] The compositions of these three products which form natural cements are as follows:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	H_2O
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pozzuolana	45–60	15–20	12–20	6–9	4–6	4–6	8–10
Terra di Santorino	68·5	13·3	5·5	2·4	0·7	7·7	1
Trass	55–58	22–24	0·7–1·6	2·5–3·9	1·3–1·8	4·5–9·6	3–7·5

the importance of the earth of Santorino for the preparation of modern cements. These products, which are generally known as hydraulic cements, do not harden under water, even if finely powdered, but acquire this property on mixing them with fat limestone, without the necessity for previous baking. For instance, 1 part of the natural cement may be mixed with 1 to 2 parts of lime and 1 part of sand.

ROMAN CEMENT. This product is obtained by calcining argillaceous limestone containing much silica mixed with coke in continuous furnaces, but maintained at a temperature lower than that of a lime-kiln and always below the melting-point of the mixture. In this way all the CO_2 is driven off, but the whole of the lime should not combine with the silica and alumina. Since the ground, finished product contains uncombined calcium oxide, it becomes slightly heated on mixing it with water, but hardens rapidly, even in fifteen minutes, though it gives a product less resistant than Portland cement. For masonry which is to be constantly covered by water it is used in the pure state, but for other work it is mixed with from 1 to 6 parts of sand. The composition of Roman cement ordinarily varies within the following limits: SiO_2, 13 to 29 per cent.; $Al_2O_3 + Fe_2O_3$, 10 to 20 per cent.; CaO, 40 to 58 per cent.; MgO, 2 to 5 per cent.

NATURAL AND ARTIFICIAL PORTLAND CEMENT

In 1756 J. Smeaton perceived that all burnt cements which contained alumina and silica, which were thus, therefore, only partly soluble in nitric acid, differed from ordinary limestones and mortars through the property of hardening even under water; this important observation was confirmed and applied practically by J. Parker in 1796. From that time attempts were made in many countries to discover natural cements, and very important deposits were actually found, especially in France, England, and Belgium. In the Grenoble mountains a seam 4½ metres thick was discovered, which from 1842 until to-day has furnished the famous cement of the Porte de France.[1]

---

[1] In Italy the first and most important region where cement-forming materials were found is that of Casale Monferrato, where more or less hydraulic mortar has been prepared from time immemorial. In 1850 there were 10 cement factories at work at Casale, and the production was about 5000 tons per annum, but the first rational cement furnace was constructed in 1859 by Costantino and Ubaldo Cerrano when the railway to Casale was laid.

The prime material was obtained from the hills of Casale, Pontestura, and especially of Ozzano, where the better limestone was mixed with layers of siliceous limestone (marly limestone), from which it was carefully separated, and the siliceous material was thrown away. It was only later, about the year 1876, that the manufacture of true Portland cement was started by utilising precisely that same siliceous and marly material which had been discarded for so many years.

It was mainly on the initiative of C. Cerrano and P. Sosso that the "Società anonima, fabbrica calci e cementi," of Casale Monferrato, was founded in 1873, and in time became the most important works in Italy for the production of natural slow-setting Portland cement, producing 50,000 tons in 1907. The share capital of this concern is £200,000. Casale cement has a tendency to set rather too rapidly, and is therefore corrected during manufacture by the addition of 2 to 3 per cent. of gypsum. The importance of the Portland cement industry in Italy to-day is shown by the statistics given later.

The surface of available limestone in Casale has been estimated at about 20 sq. kilometres, but of late years other important deposits have been found besides those of Casale, Ozzano, and Pontestura. These various deposits are superposed and were formed at various epochs, separated by centuries, at the bottom of a prehistoric sea, were then dislocated and raised by cataclysms and earth movements, and to-day the stratifications of the Casale hill dip at an angle of 40° to 60° to the horizon. The various banks of argillaceous limestone which form the available seams are 4 to 6 metres thick, and of graduated composition, which ranges from a marl for hydraulic cements with limestone of micro-crystalline structure, to a more siliceous marl for slightly hydraulic cements and a very argillaceous limestone and finally clay of earthy appearance. They do not contain free silica, and the combined silica is always present in double the quantity of the alumina and iron. The ratio between the clay and calcium carbonate is variable and the deposits are richest in clay at the lower part, and thus various qualities of limestone are obtained which are called by various local names: *marmorina* (the richest in limestone), *dura*, *bastardella*, *molle*, *magra* (the richest in clay), etc.

During the first few years the most advantageously placed deposits, that is, those nearest the surface, were exploited or excavated to a depth of a few dozen metres into the seam. For some years past, however, the exploitation of the less accessible seams has been started by excavating galleries several hundred metres long and shafts down to a depth of 100 metres. For this reason the prime material costs more than double as much as that first obtained, namely, up to 6*s.* 5*d.* per ton at the works.

It is generally considered that the Casalese deposits belong to the upper layers of the eocene period, and it is probable that they originally had a thickness of 1000 metres or more. It is now maintained by others that these deposits do not belong to the eocene, but to the miocene

So far only natural cements obtained by burning argillaceous limestone had been considered,[1] but Vicat in France showed by a series of experiments, started in 1812 and continued for many years, that still better cements, which set more rapidly, could be prepared artificially from mixtures of suitable chemical composition. Important practical applications of these studies were made in England in 1824 by J. Aspdin, who obtained a high-class hydraulic cement which he called *Portland cement* by heating a mixture of slaked lime and clay to a very high temperature. He called it Portland cement because on treatment with water it formed a hard mass of similar colour to the Portland stone which was at that time highly prized for building purposes in England.

From that time the Portland cement industry developed very greatly in England. The first French works was erected in 1850 and the first German works in 1852. In Italy the first attempts were made at Palazzolo in 1858, and these have led to the formation of a great national industry of recent years, the principal centres of which are in Bergamasco,[2] at Ponte Chiasso in Como, in Venetia, and to-day also in various other parts of Italy. In all these places modern plants and perfected machinery are used.

The first chemical investigations of the cement showed that this was almost entirely formed of calcium silicate and aluminate, together with iron, magnesium, and alkali silicates as impurities. It has also been found that the best qualities of natural cement contain the lime, alumina, and silica in very definite proportions, varying within narrow limits. There is generally limestone (calcium carbonate) and clay (aluminium silicate) mixed so intimately, almost molecule to molecule, that no machinery could mix it more completely. On burning at 1300° to 1400° carbon dioxide is evolved and a partial chemical combination occurs between the lime, alumina, and silica, as soon as the mass is simply sintered by the heat, and not fused. The resulting product has very great powers of reaction with water, with which it sets and generally forms very stable and compact

---

period, and they deduce this from the fact that imprints of fossil shells, characteristic of the latter period, are sometimes discovered in the seam. These imprints are, however, extremely rare and certainly doubtful. Others also do not admit that the actual position of these seams is due to upward displacement caused by earth movements, but to other causes which have not yet been properly determined.

Not long ago a calcareous deposit was discovered in Dalmatia, suitable for slow cements. According to the geologists, this also belongs to the eocene period and differs from the Casale deposits in the fact that these seams are 20 metres thick and are considerably more homogeneous chemically than the Monferrato deposits.

[1] The compositions of certain natural rocks, argillaceous limestones, marls, etc., used for natural cements are :

	SiO_2	Al_2O_3	CaO	CO_2	MgO	Fe_2O_3
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Stone for Portland cement . .	12·05	20·3	34·58	27·17	—	3·0
,, from Porte de France (slow) .	15·8	26·6	28·91	22·72	0·20	—
,, ,, Palazzolo (slow) . .	7·7	12·9	40·72	32·50	1·00	2·0
,, ,, Casale Monferrato .	11·1	18·7	33·21	26·50	1·20	4·0
,, ,, the shores of the Black Sea	13·5	4·8	44·40	35·00	0·10	1·35

[2] The first attempts to manufacture artificial Portland cement in Italy were made at Palazzolo on the Oglio in 1858, but were only successful about the year 1864. In 1865 the Ministry of Public Works prescribed the use of the products of the new "Società Bergamasca per la fabbricazione dei cementi e delle calci idrauliche" for all public works, and this company thus became the powerful "Società italiana dei cementi e delle calci idrauliche di Bergamo," with various works at Villa di Serio, Pradalunga, Comenduno, and Palazzolo on the Oglio (1872). In the last works, since 1877, apart from the preparation of hydraulic cements, a great impetus was given to the manufacture of artificial Portland cement by coarsely grinding a mixture of marl and pure limestone obtained from the hill on the Lake of Iseo, and then adding by means of an automatic balance a definite quantity of the lime produced as a residue in the manufacture of hydraulic cements. It is not necessary to dry this mixture, because the quicklime serves as a drying agent, and it is finally ground in a tube mill (*see below*), and is then moistened and transformed into bricks, which are dried in the air under a shed for a couple of months. After this it is dried, baked in Dietzsch furnaces, and then ground in the usual manner (*see below*).

The Società di Palazzolo amalgamated in 1906 with the works of Pesenti Brothers with a total share capital of £240,000 and a possible output of 300,000 tons per year of hydraulic, natural, and artificial Portland cements.

hydrates, insoluble in water, and almost unattacked by dilute acids.[1] Sea water slowly attacks cement structures which are not constantly immersed (*see later*) and solutions of calcium sulphate are still more harmful.

Artificial Portland Cement has acquired great importance in recent years, especially outside Italy, and more particularly in Germany and in the United States. Thus in Germany the Government prescribes the employment of artificial cement for many public

---

[1] *Theory of the setting and hardening of cement.* Cut and polished plates of Portland cement were microscopically examined almost simultaneously in 1897 by Törnebohm and by Le Chatelier, and led to the discovery of four fundamental components of cements:

(1) *Alite*, $8CaO, 2SiO_2, Al_2O_3$ (Jänecke, 1911), is the most abundant. It forms colourless crystals which are very refractive, feebly doubly refractive, and of rectangular or hexagonal section.

(2) *Belite* has a dirty yellow colour and is slightly opaque; it shows vivid interference colours. It has two optic axes and its refraction is fairly strong. It forms small round grains without recognisable crystalline form. These are occasionally striated, sometimes in two directions which cut one another at variable angles.

(3) *Celite* is of a deep orange-yellow colour. It is strongly doubly refractive. It is sometimes present in the form of small rods, especially in cements which have been only slightly burnt. In well-burnt cements it forms a filling between the other elements of the stone and gives the cement its colour, because it contains a maximum quantity of iron. It consists principally of calcium aluminate, which melts slightly above 1400 and is then able to dissolve calcium orthosilicate and CaO.

(4) *Felite* is colourless, has two optic axes and shows very strong double refraction. Its refractive power is about equal to that of belite. This mineral is present in the form of rounded grains which have sometimes a slightly lengthened shape, but do not show crystalline contours.

Apart from these four minerals, Törnebohm recognised the presence of a mass which was probably amorphous and isotropic, colourless, and very strongly refractive, being superior to alite in this respect. It forms a filling between the minerals and is not always easily distinguishable from alite.

From the chemical point of view the most recent and likely hypotheses to explain the setting and hardening of cement are the following:

According to Rohland (1909) the setting and hardening occur because the lime in burnt cement is in a state of solid solution or rather of "absorbent combination." When it is worked up with water, the cement separates the silica, iron oxide, and alumina in the form of colloidal hydroxides which are coagulated by the calcium hydroxide which is simultaneously separated by hydrolysis. The more colloidal substances are present, the more carbonate can be formed by the lime with CO_2.

According to E. Stern, crystallised calcium hydroxide is present abundantly in hardened cements, together with dry colloidal substances already observed by Bucca and Oddo in 1896, by Törnebohm in 1897, and by Michaelis in 1901. In fact the calcium aluminate of the cement may be decomposed by water forming crystalline calcium hydroxide and gelatinous aluminium hydroxide, and this may be shown by shaking up cements or specially prepared pure calcium aluminate with water and pouring the whole on to a filter. Calcium and aluminium are then present in the filtrate, and if this liquid is exposed to dialysis, calcium passes through the dialyser without any trace of alumina, because the latter is present in the colloidal condition.

In the first phase of the phenomenon of setting through the action of water, the colloidal substance formed, which is probably aluminium hydroxide, envelops each granule of cement, at the surface of which many hard crystals of calcium hydroxide are gradually formed. The phenomenon of hardening is thus started and is accompanied by the formation of other crystals of calcium aluminate and silicate occluded in the gelatinous mass.

That calcium hydroxide is present in hardened cement is argued from the fact that on dialysing it in the state of a suspension of the powder in water, lime only is found in the liquid which passes through the membrane, whilst a flocculent colloidal residue, richer in silica and alumina, but poorer in lime than the original cement, is left above the membrane.

Crystals of calcium carbonate are always found together with those of calcium hydroxide, and are formed by the action of the carbon dioxide which is always present in the water used. The colloidal matter protects the crystals of calcium hydroxide from the action of the water in structures formed of hydraulic cement; the lime would otherwise be gradually dissolved by the water.

In any case, the phenomenon of setting and hardening presents problems which are not yet completely solved.

It has been noted that cements which are very rich in alumina set more rapidly, and the manufacturers obviate this disadvantage by adding 1 to 2 per cent. of natural gypsum, or sometimes even calcium chloride, to the burnt cement before grinding.

The action of $CaSO_4$ or of $CaCl_2$ on the setting of cement was explained by Candlot by the formation of a double compound of gypsum and calcium aluminate as soon as these are brought into contact with water (it is the calcium aluminate which causes rapid setting). The compound formed is $(Al_2O_3,3CaO + CaSO_4)\ 30H_2O$, or $(Al_2O_3,3CaO + 2CaCl_2),\ 16H_2O$, which is crystalline and insoluble. It may also be that the gypsum retards the setting, because it renders the calcium aluminate less soluble and thus less liable to react with water.

works, because by means of the perfected machinery introduced into this industry to-day products are obtained of which the constant composition and properties can more certainly be relied on.

Selection and Proportions of Prime Materials for Cement Manufacture. Theoretically, in the case of pure materials, it would be necessary to mix 19 to 20 per cent. of clay with 80 to 81 per cent. of calcium carbonate in order to obtain a Portland cement on burning. In practice, in order to prevent any excess of lime (even 0·5 per cent. more than is necessary may be harmful to the finished cement when used), a little more clay is added, so that ordinarily, according to the nature of the prime materials, 20 to 25 per cent. of clay and 75 to 80 per cent. of limestone are used. Excess of clay may also be prejudicial during burning, as dicalcium silicate may be formed instead of tricalcium silicate, and this increases the friability of the cement, even in the furnace itself, so that during cooling it is easily transformed into powder.[1]

Except in those cases in which the marl or stone gives a cement in which the clay and limestone are naturally present in the right proportions, it is necessary to correct the natural marl or to add the prime materials to one another from the first in exactly the right proportions to form artificial cement, bearing in mind the type of cement which is desired, and with which a definite hydraulic index (*see above*) corresponds.

In the case of **Slow-setting Cements**,[2] the hydraulic index, x, varies from 0·45 to 0·60, and in **Rapid-setting Cements** from 0·6 to 1·2. The value of x may always be calculated by introducing the percentages of the various compounds as found by an accurate analysis into the following formula:

$$x = \frac{Al_2O_3 + Fe_2O_3 + SiO_2}{CaO + MgO + K_2O + Na_2O},$$

but ordinarily the alkali, $K_2O + Na_2O$, is neglected in this calculation. Some use the *hydraulic modulus*, which is the inverse of x, that is:

$$y = \frac{CaO + MgO + K_2O + Na_2O}{Al_2O_3 + Fe_2O_3 + SiO_2}$$

and here also the quantity of alkali is often neglected. y varies within the limits 0·8 to 2·2. Thus, if we indicate the quantity of iron and aluminium silicate in the limestone by S_1, that of the clay by S_2, of the lime and magnesia of the limestone by C_1, and the lime and magnesia of the clay by C_2, then given the modulus, y, which is required, the relation between the limestone and clay is given by the general formula $\frac{yS_2 - C_2}{C_1 - yS_1}$, which is

---

[1] This disadvantage may be prevented by keeping the temperature a little lower in the furnace and thus avoiding a softening of the red-hot mass, but then a larger quantity of calcium aluminate remains, which causes the cement to set more rapidly, and thus as a mortar it makes less resistant brickwork, but all the same does not undergo any deformation and does not give cracks as is the case with cement containing an excess of lime.

[2] Those cements are called slow-setting cements which set in the form of mortar within 10 hours by the needle test of Vicat (*see below*), and a wall constructed with such cement is thoroughly resistant after 8 days, although the hardening continues slowly, and in a year or a little more the whole mass acquires the same hardness as the most compact stone.

Rapid-setting cements set in from 2 to 3 minutes, although the best qualities require from 6 to 10 minutes.

It has been noticed in practice that various causes influence the rapidity of setting. the temperature of the water and of the atmosphere (climate), the nature of the water used in making the mixture, the quantity of water used in the paste, etc.

If a cement or a mortar is used after the period of setting has already started or ended, it no longer has the necessary resistance, and it is a mistake to powder and re-employ such dead cement, because when once it has reacted with the water, it no longer has any value. For this reason it is obviously necessary to preserve powdered cements in dry localities.

The hydraulic index for contracts in France may vary between 0·42 and 0·48 (or 0·47 for a cement containing 8 per cent. of alumina), but must be diminished by 0·02 for each 1 per cent. of alumina below this figure. Those cements are considered less good which have hydraulic indices up to 0·60. Of two cements of equal hydraulic index, the one which contains the more silica sets the more slowly, and the one containing more alumina sets the more rapidly. It sometimes occurs that the rapidity of setting of a cement increases simply through the fact that it has become heated in the sun or in the trucks in which it is transported.

sufficiently close for use in daily practice[1] if care is taken that materials containing much magnesia or calcium sulphate are rejected, because they form a less resistant cement. When there is a deficiency of iron the prime materials are corrected by the addition of burnt pyrites, and if there is an insufficient quantity of alkali, wood ashes are added, because the alkalis both act similarly to lime and magnesia, that is, lower the temperature of fusion and of reaction of the silica, and also form cements which set more rapidly. In clay which is to be used for cements it is only the combined silica, and not the free silica, which is of value, therefore in some cases it is better to eliminate the latter by suitable levigation. The composition of Portland cement varies within the following limits[2]: $SiO_2 = 20$ to 26 per cent.; $Al_2O_3 + Fe_2O_3 = 7$ to 14 per cent.; $CaO = 57$ to 65 per cent.; $MgO = 0{\cdot}3$ to $2{\cdot}5$ per cent.; alkali $= 0$ to $1{\cdot}2$ per cent.; SO_3 (sulphates) $= 0$ to 3 per cent. Cements containing the most silica set slowly, whilst those containing much alumina set rapidly.

It is clear that in the analyses, both of the prime materials and of the finished cement, the silica content must be understood to be combined silica and not free or quartzose silica, which takes no part in the formation of the cement.[3] In argillaceous limestone which is to be used in the manufacture of cements, the portion insoluble in acids should be completely soluble in alkali, otherwise it consists of free silica or quartzose sand.

MANUFACTURE OF ARTIFICIAL CEMENT. This industry has to-day acquired so much importance in all civilised countries, and is connected with such important technical problems, chemical, physical, and mechanical, that it deserves to be treated in greater detail than usual in order to give chemical students an idea as to which factors conduce to perfection and to industrial

---

[1] If we have prime materials giving the following figures on analysis:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali	CO_2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Clay . .	55·7	17·2	8·3	1·4	2·4	1·6	3·3	10·1
		81·2						
Limestone .	2·5	1·4	1·1	53	0·2	—	—	41·8
		5·0						

we have the following values: $C_1 = 53{\cdot}2$; $C_2 = 3{\cdot}8$; $S_1 = 5$; $S_2 = 81{\cdot}2$; if now we wish to obtain a cement with a hydraulic modulus, $y = 2$, the ratio between the limestone and the clay will be the following:

$$\frac{(2 \times 81{\cdot}2) - 3{\cdot}8}{53{\cdot}2 - (2 \times 5)} = \frac{158{\cdot}6}{43{\cdot}2} = 3{\cdot}7,$$

that is to say, 1 part of clay must be mixed with 3·7 parts of limestone, and this ratio must be altered a little if we take the alkali also into account.

[2] We here give the mean composition of cements produced in various countries:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Hydraulic index
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
French cement	21–26	5–8	2–4	57–68	0·7–2	0·48–0·54
English ,, ...	20–24	6–10	2·4–5	59–63	0·3–1	0·47–0·60
German ,, ...	20–25	5–11	2·5–5	58–68	0·9–2	0·46–0·58
Belgian ,, ...	23–26	5–9	2–4	60–65	0·6–1	0·49–0·59
Russian ,, ...	21–23	6–8	3–4	62–65	1–2	0·47–0·52
Casale Monferrato cement I .	22·73	8·64		64·04	1·40	0·47
Casale Monferrato ,, II .	23·47	8·59		63·60	1·48	0·49
Palazzolo ,, .	21·45	9·15		63·12	1·48	0·47
Civitavecchia ,, .	24·60	11·35		58·75	1·54	0·59

[3] F. Coppola, of the Torres Works at Vittorio, maintained (1909) that a cement of good quality may also be obtained by starting from an argillaceous limestone rich in active silica (quartzose silica insoluble in acids and in alkalis), if sufficiently finely ground, because the inactive silica then becomes active during burning.

progress, and how apparently secondary or comparatively unimportant factors may in many cases decide the life and future of an industry. Each operation must be conducted with the maximum precision and studied in all its smallest details in order to obtain the best results, and if possible arrive at improvements. We shall now treat shortly and clearly of the principal operations connected with the preparation of cements, some of these being common to the preparation of both the natural and artificial product.

GRINDING OF THE PRIME MATERIALS. The very finest grinding and intimate mixture of the limestone and clay are of great influence on the good qualities of the final product.

In the past the materials were exclusively ground by dry methods, but to-day wet grinding has in many cases been advantageously applied.

(*a*) **Dry Grinding.** In order to pulverise the two prime materials, clay and limestone, finely, it is indispensable that they should be thoroughly dry (less than 4 to 5 per cent. of moisture), otherwise in modern ball mills the ground powder will form lumps, which render the work irregular and difficult and lower the yield.

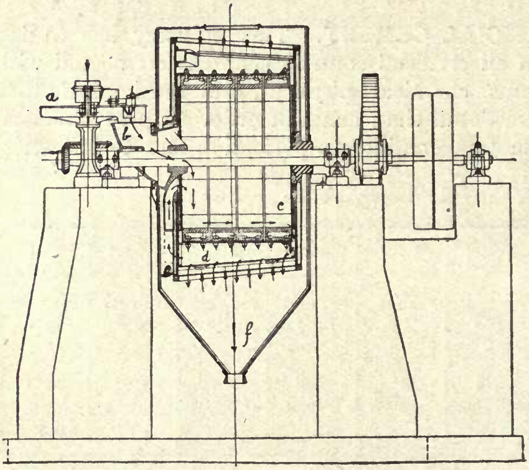


FIG. 289.

The prime materials are dried in a species of conical brickwork tower, being charged in above and discharged at the base, whilst a current of hot air passes into the lower portion of the tower. Finely divided materials may also be dried in rotary iron cylinders inclined at a very slight angle to the horizontal, the material to be dried entering continuously at the top and issuing at the base, being met by a current of hot air, which passes in from below.

The limestone, before or after drying, is coarsely crushed in a rock-breaker (*see* Fig. 100, p. 292), which crushes up to 15 tons per hour with a minimal expenditure of energy. At one time the material was finely crushed by pressing it between two laminated cylinders and then pulverising it in mills with two horizontal stones, such as were used in old-fashioned flour mills. A minimal production is, however, thus obtained (less than 1 ton per hour) and very much power is required (20 to 30 h.p. per mill), and therefore ball mills were resorted to with advantage about 20 to 25 years ago, and were soon generally used in all works (*see* Figure and description on p. 651). Since 1900 the work of the ball mills has been modified in the direction of first producing a kind of coarse flour, and then completing the fine grinding in other apparatus. Ball mills with sieve plates Nos. 70 to 80 (*see* p. 651) gave 2 tons of finest limestone powder per hour, but required up to 40 h.p.; now, on the other hand, a plate with larger meshes, Nos. 20 to 25, is used, and with an equal consumption of power 6 tons of limestone are treated, the final grinding being then completed in tube mills. In 1900 F. L. Smidth, of Copenhagen, constructed a small improved ball mill called a "kominor" (Figs. 289 and 290) in which the plates of the internal drum are not perforated, and thus the meal to be ground, which enters at the one end, *a* and *b*, is slowly transported by the rotation of the drum to the opposite end before passing into the exit fissure, *c*, and thus remains in contact with the steel balls for a longer time and pursues a longer path, dependent on the size of the kominor, which may be up to 2 or 3 metres. The balls are of hard steel weighing 2 to 3 tons in all, and have a diameter of 5 to 12 cm. A larger production of meal is thus obtained for the same consumption of energy or greater fineness for an equal production. The fineness may be increased at will by diminishing the production. On escaping from the drum the meal falls on to a conical sieve, *d*, which surrounds the drum, and the fine meal is thus collected in *f*, whilst the coarser portion which remains on the sieve is carried to its extremity, *e*, from where the rotary movement of the drum and of the sieve carries it back into the drum again to pass again through the ball mill. The yield of the kominor is 20 per cent. greater than that of the old ball mills. It requires fewer repairs and may also be constructed in very large sizes, up to 5 tons weight of balls. By diminishing the production one may also dispense with the sieve. With 1·2 ton of balls, 1·8 ton of meal may be obtained per hour, passing through sieves Nos. 20 to 25, and 20 h.p. is then used. A kominor, the weight of the balls of which is 5 tons, requires 85 h.p. Ball mills similar to the kominor have been given various names by the various firms who construct them (Krupp, Löhnert, Pfeiffer, etc.); the firm of Smidth alone constructed up to 1909 500 kominors for various cement works throughout the world.

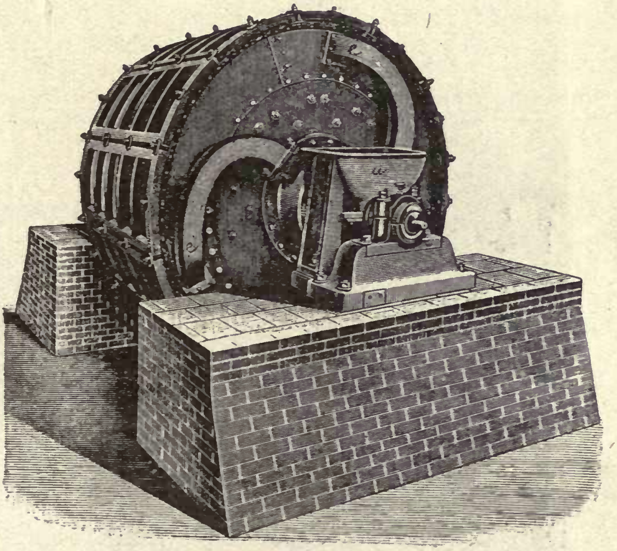


FIG. 290.

The limestone and clay which have been reduced to meal by ball mills or by the kominor then undergo finer grinding in the tube mills or Dana tubes, or by means of pneumatic separators, which separate the finest flour already contained in the meal by means of an air-blast, and regrind the coarser meal. These pneumatic separators are connected directly with the kominor and require very little power—5 to 6 h.p.

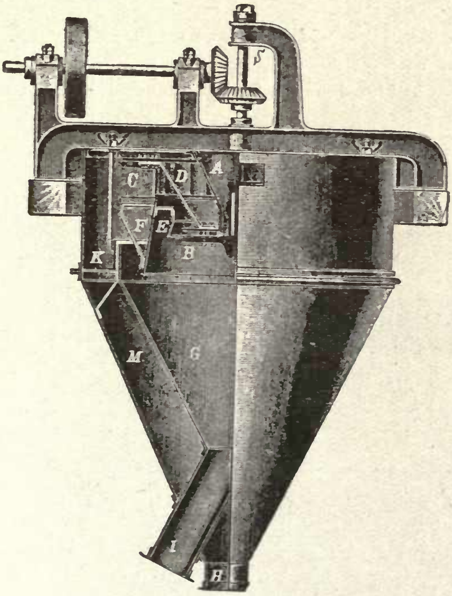


FIG. 291.

The *pneumatic separator,* as it is constructed, for instance, by the firm of Pfeiffer (Mumforde Moodie patent), consists essentially of two large concentric cones of sheet iron pointing downwards (Fig. 291). The meal which is discharged by the kominor is carried by bucket elevators into the hopper, *A*, of the separator, whence it falls regularly over a horizontal plate, *B*, supported by a vertical shaft, *S*, actuated by cog-wheels. On this plate arms, *D*, are fixed, carrying peripheral blades, *C*, which act as a fan when the plate revolves. The meal is thus projected from the plate through the slits, *E* and *F*, and the strong current of air caused by the fan carries the finer powder to the wall of the larger cone, *K*, at the base of which it collects and is discharged through the opening, *H*, whilst the coarser portion of the meal passes only into the smaller cone and is discharged below through the opening, *I*, being then returned to the ball mill (*see* Figs. 292 and 293, view and section of the plant, including a kominor and pneumatic separator with bucket elevator). The fineness of the product collected in *H* is increased on diminishing the velocity of the fan, which thus causes less flour to pass over the regulator, *K*, so that more is returned to the mill.[1]

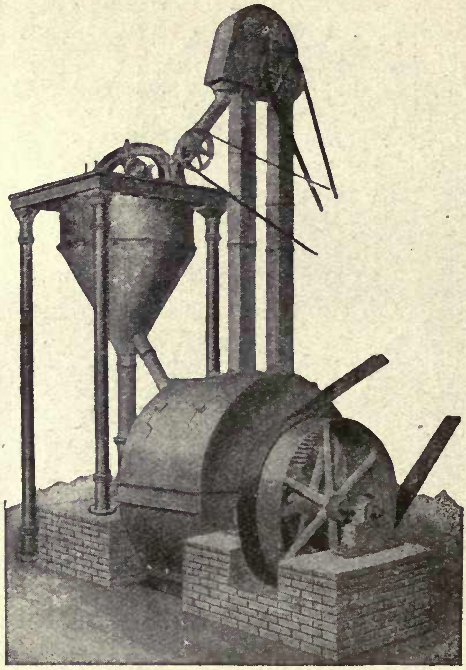


FIG. 292.

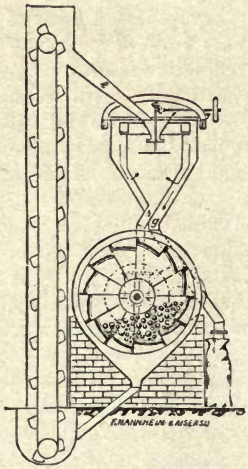


FIG. 293.

Tube mills or *Mill tubes* or *Dana tubes* are still more widely used than pneumatic separators for the production of the finest powder without the need of sieves from the meal of the ball mill or kominor. On crushing a grain of limestone of 10 mm. diameter 1000 grains of 1 mm. diameter may be formed, or 1,000,000 grains of $\frac{1}{10}$ mm. diameter. Although, at first, in order to crush the larger grains mills with few but large and heavy balls are

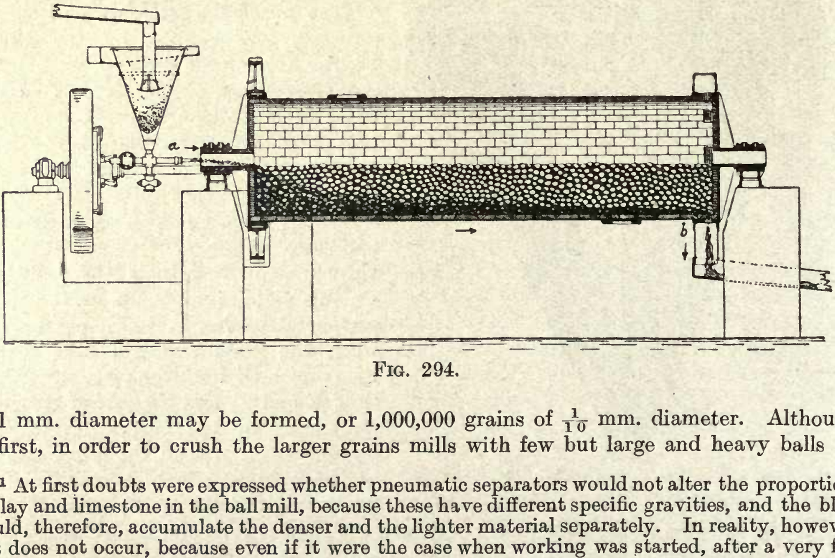


FIG. 294.

---

[1] At first doubts were expressed whether pneumatic separators would not alter the proportions of clay and limestone in the ball mill, because these have different specific gravities, and the blast would, therefore, accumulate the denser and the lighter material separately. In reality, however, this does not occur, because even if it were the case when working was started, after a very few minutes of continuous feeding in of meal of definite composition from the kominor, the conditions inside the apparatus must soon establish such an equilibrium or proportion between the two materials of different nature that the fine powder assumes the same composition as the meal.

required, for the final pulverisation of the numerous small grains smaller spheres will be required, but in great numbers, that is, one requires a larger grinding surface and a prolongation of the time of contact of the grinding balls with the meal which is to be powdered. The idea of tube mills simply formed of long horizontal iron tubes half-filled with large numbers of small steel balls or hardest flints arose from this consideration (Figs. 294 and 295).

Tube mills are now constructed up to 10 metres in length of a diameter of 1 to 6 metres, which are charged with 15 tons of flint pebbles and make 8 to 12 revolutions per minute, absorbing 80 to 100 h.p. The internal surface of the tube is lined with hardened steel or with very hard flint tiles. The meal to be ground enters through the tube *a*, which acts as a hollow pivot for the cylinder, and passes out through a peripheral opening provided with a grid at the opposite end of the tube. As is seen in Fig. 294, the quantity of meal, indicated by dark shading, *b*, diminishes gradually as it approaches the exit opening, whilst the quantity of steel balls remains the same at all points, so that as the meal is ground the proportion of spheres constantly becomes greater compared with the quantity of meal to be pulverised. The fineness may be increased at will by diminishing the quantity of meal which enters. The product escaping does not need to pass through a sieve, but is already so fine that sieves with 900 meshes per square centimetre do not retain more than 1 to 2 per cent., and sieves with 4900 meshes per square centimetre less than 25 per cent.

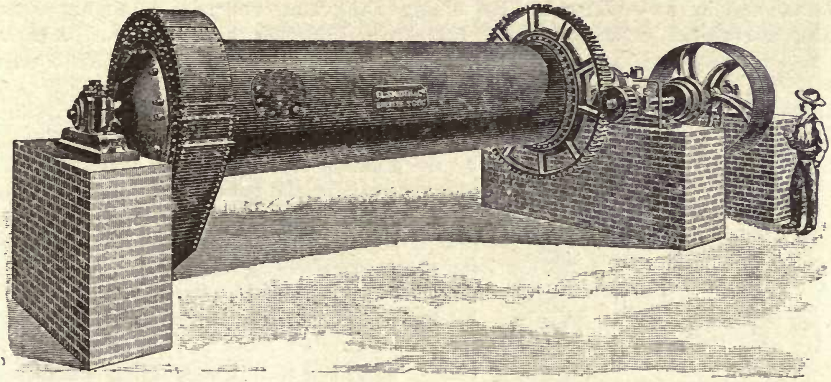


FIG. 295.

(*b*) **Wet Grinding.** This was first applied to friable or powdery limestone and to clay which was mixed with pebbles and coarse sand, introducing it in the necessary proportions, together with water, into a large circular brickwork vat, *A* (Fig. 296), in the centre of which is a small pillar supporting a revolving head carrying horizontal iron arms, from which a sort of very heavy harrow was supported by chains and dragged along the bottom of the vat on turning. After 30 to 50 minutes all the pebbles and heavy sand were deposited at the bottom, whilst the clay was transformed into a liquid paste supported in the agitated water, and was discharged into the vat *B* placed below, through a metallic sieve, which retained the stones and coarser sand. In the second vat the paste was remixed by stirrers, and in the meantime samples were removed for rapid analysis in the laboratory (by determining the carbon dioxide of the carbonate), and if the relation between the clay and the

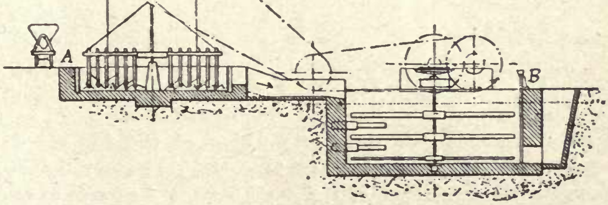


FIG. 296.

limestone did not correspond with the required values, a definite quantity of another paste, richer in limestone or clay, was added from another vat always kept in readiness. This paste was passed by a suitable pump into tube mills which work very well even with a wet mixture, and give a finer product than when a dry mixture is used; only 15 per cent. remains on a 4900 mesh sieve. If the paste which escapes from the tube mill has been prepared with 35 to 38 per cent. of water only, then it may be directly passed into rotary kilns; if, on the other hand, vertical kilns are used, the paste must be allowed to settle and the water decanted and the mass then dried slowly and converted into bricks, as will be described below.

The firm of Smidth of Copenhagen advises the grinding even of hard limestone directly in the wet way in the kominor, and the mixing of the calcareous paste with a clay suspension in the required proportions before being passed through the tube mills. Tube mills are constructed by the same firms which construct ball mills and the kominor (*see above*).

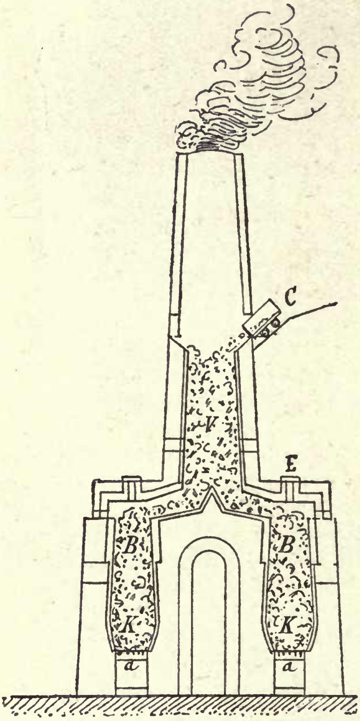


Fig. 297.

CEMENT-BURNING KILNS. The intimate mixture of limestone and clay having been obtained by the grinding machinery, it is necessary before burning to shape the powder into bricks by mixing it with 8 to 10 per cent. of water and passing it into ordinary brick-making machines; that used for the preparation of fuel briquettes, as already described on p. 459, also serves very well. The bricks are allowed to dry in the air under cover for some weeks, or are preferably placed on cars and then dried by hot air in a long drying chamber.

At this point the burning and the subsequent operations are the same for either natural or artificial cements. The temperature of burning (incipient fusion) is 1300° to 1400°, although the engineer Bonde, of Copenhagen (1909), has shown that the best results are obtained at 1500°.

The first continuous kilns to be used in large cement works were the *stage kilns of Dietzsch,* more or less modified, which led to considerable economy of fuel compared with the old intermittent kilns (from 25 to 30 kilos of coke per 100 kilos of cement the amount of fuel was reduced to 14 to 18 kilos). In Fig. 297 we see the original form of Dietzsch kiln. The charge was introduced by means of cars, *C,* and consisted of alternate layers of coal and of dried bricks of cement or of the natural cement-forming rock, and fell into the two or more lateral chambers, *BB,* of the kiln, which terminated below in grates, *a, a,* these supporting a portion of the weight of the charge. When the combustion was once started through the openings, *E,* in the platform above the two lateral chambers, the regular working of the furnace was soon established and the coal was completely burnt, so that the maximum temperature was produced in the upper part of the chambers, *B,* and drew in a current of air through the grates, *a,* whilst the hot gas escaping through the chimney dried and preheated the materials which were charged into *V* as fast as corresponding quantities of burnt cement were discharged below by removing a few bars of the grate, *a.* The burnt cement discharged below was almost cold, because the cold air which entered through *a* to sustain the combustion in *B* cooled the burnt cement in *K;* thus also the heat remaining in the burnt cement was utilised, and it was possible to attain the necessary temperature of 1400° to 1500° to soften and partially to fuse the crude cement. The passage of the material from the chimney, *V,* to the chambers, *B,* was facilitated by long iron shovels worked by operators through the various openings of the furnace, and enabling the combustion to be sustained by the addition of coal through the opening, *E.* Such a kiln gives about 15 tons of cement per 24 hours.

The Schöffer or Aalborg kilns were first used at Aalborg in Denmark, and then in other countries, and were found to be advantageous (Figs. 298 and 299). The material is charged in at the top at *A*, and the furnace is constricted at *B* to a cone, and is thus better able to support the weight of material which afterwards enters the combustion chamber, *C*. The furnace is again enlarged at the cone, *D*, where there are several inclined flues, *K*, through which the fuel (long-flaming coal) is charged, and the material is removed with long iron tools when it is to be discharged through the lower grate, *R*. The consumption of fuel in these furnaces, which yield 15 tons of burnt cement per twenty-four hours, is 13 to 15 kilos for each 100 kilos of cement. The kiln is lined internally with refractory bricks which sometimes last two years, during which time the furnace is in uninterrupted work without the necessity for any repairs.

In Italy and France certain works use an analogous kiln (the Perpignani-Candlot) in which the life of the firebricks is prolonged by placing round them an air-circulation chamber which cools them and prevents them from sticking. The fire-hearth is circular with vertical bars.

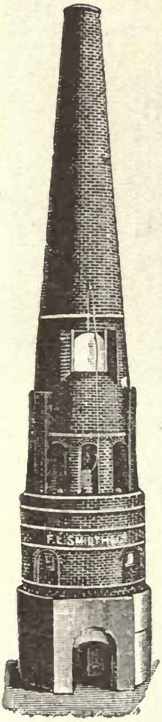


FIG. 298.

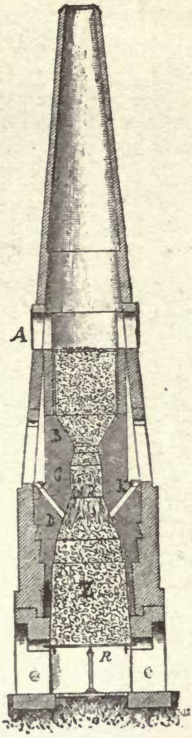


FIG. 299.

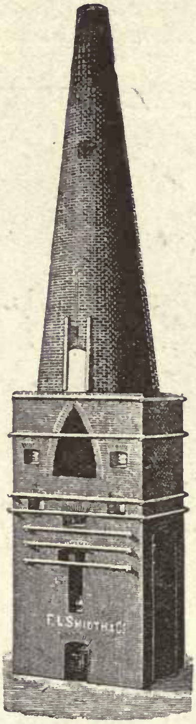


FIG. 300.

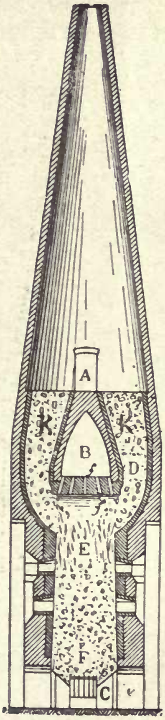


FIG. 301.

Another form of cement kiln which has partially replaced the Aalborg kiln is the Rysager or R-kiln, first applied in Denmark by the firm of F. L. Smidth of Copenhagen. It has almost the form of an inverted Dietzsch kiln (Figs. 300 and 301). There are two drying and preheating chambers, *KK*, leading the material charged in at *A* into the single heating chamber, *E*, into which the coal is charged through various passages, *f*. In this way the maximum temperature is not obtained near the furnace walls and the refractory lining is thus better preserved, avoiding clogging of the cement, which is facilitated by coal ash which acts as a flux. The cold burnt cement is discharged in the usual way by removing several bars of the grate, *C*. With this kiln three workmen are required by day and three by night for all necessary operations, and the consumption of coal is 12 to 14 kilos per 100 kilos of burnt cement.

In Italy, especially at Casalmonferrato, use is made of the Palena kiln, similar to the R-kiln.

The burnt cement produced in the kiln is called *clinker*.

In general cement burnt with coal poor in ash is better than that burnt with coal rich in ash.

Fig. 302 shows the exterior of a cement works. *A* is the drying tower for the clay, *B* the two towers for drying the limestone, which arrives along an overhead ropeway, *C*, and *D* are the chimneys of the kilns, *R*, for burning the cement, which pass through the roof of the works.

ROTARY KILNS. Amongst all the great improvements introduced into the cement industry of late years, the most remarkable is certainly that of the application of rotary kilns.

These kilns allow the cement to be burnt without any necessity for first forming it into bricks or for previously drying the mixture. The latter is introduced directly into the furnace in the form of a slightly moistened powder containing 8 to 10 per cent. of water, or as a liquid paste containing 30 to 33 per cent. of water.

The first attempts on a small scale to apply these rotary kilns were made by Ransome in England in 1885 without success, whilst a little later, about 1890, they were successfully applied in the United States by using as fuel heavy petroleum oil, atomised in the furnace itself.

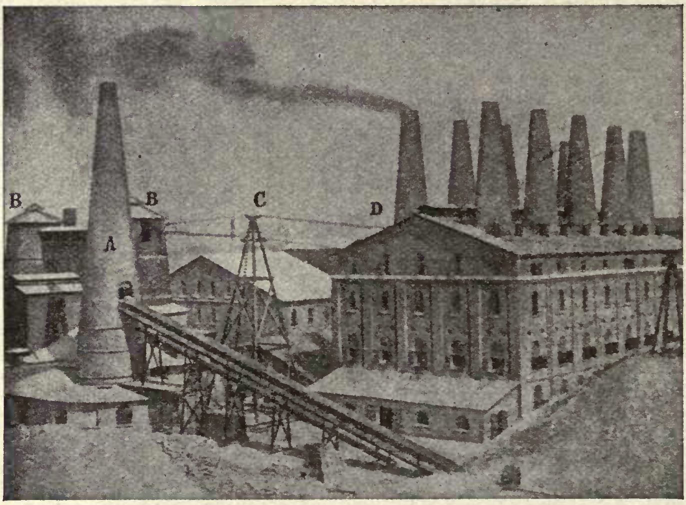


FIG. 302.

In 1895 to 1897 Hurry and Seamann of the Atlas Cement Company of Northampton, Pennsylvania, replaced the petroleum residues by finely pulverised coal (powdered in tube mills), and it then became possible to apply rotary kilns also in Europe. The first plants, after the attempts of Forell and Lollar in Germany, were constructed by the firm of Smidth at Aalborg in 1898 and by Dr. Prüssing of the Brennofen Bauanstalt of Hamburg in 1899.

These first rotary kilns were 10 to 20 metres long, but to-day they are built 45 metres or more in length and 2 to 2½ metres in diameter, especially if the material is to be charged in as a soft paste containing much water.

The large cylinder of the rotary kiln (Figs. 303 and 304) is inclined at an angle of 4° to 6° according to the degree of moisture in the paste. It is mounted on large pillars and revolves on loose rollers. It is constructed of large riveted iron plates which are lined internally—especially at the burning zone, *B*—with refractory bricks or special bricks made of cement and clinker.

The upper part of the tube *A* leads into the smoke flue connected with the chimney through which the steam formed by the drying of the paste continuously passes from the upper part of the tube above *A* and is carried away.

The cylinder is rotated at the rate of one to two turns per minute, and this carries the mass of crude cement slowly downwards. It forms granules of the size of walnuts and peas, and is gradually dried and heated by dry, finely powdered coal, which is blown in at the lower end of the tube at *B* (Fig. 304). This coal is powdered in a small kominor and a small tube mill or with a pneumatic separator. It burns completely and instantaneously. The hot air by which the coal is blown in, and by which it is burnt, passes in through the tube *O* from the cooling cylinder for the burnt cement, *D*, which consists of a revolving cylinder inclined towards the kiln through which the semi-fused cement falls in separate granules. A large fan cooled by a current of water is placed at the top of the cooling cylinder, and draws in a current of cold air through the red-hot clinker; the air is thus gradually heated by the agency of the clinker, and then blown in to the coal at a temperature of 200° to 300°.

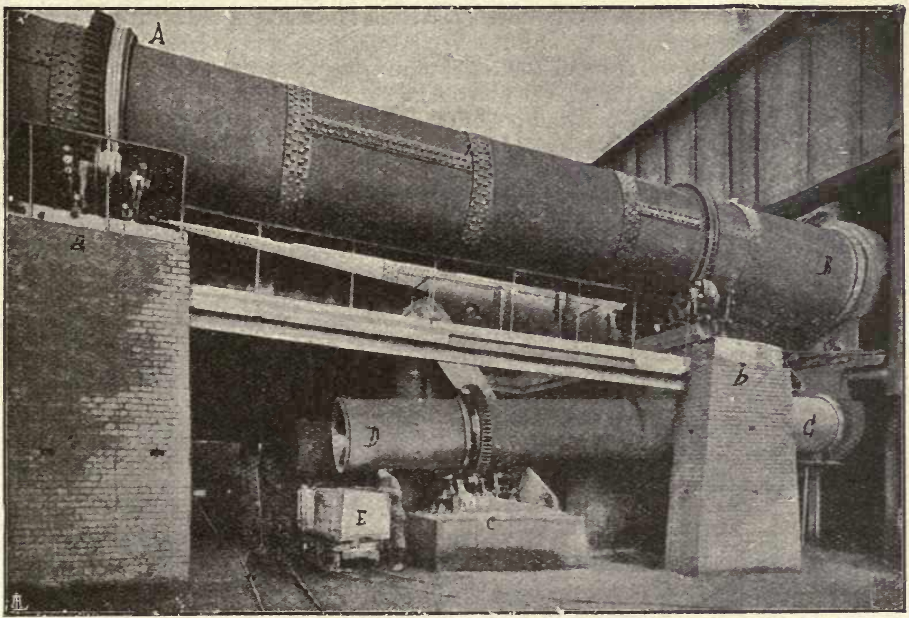


FIG. 303.

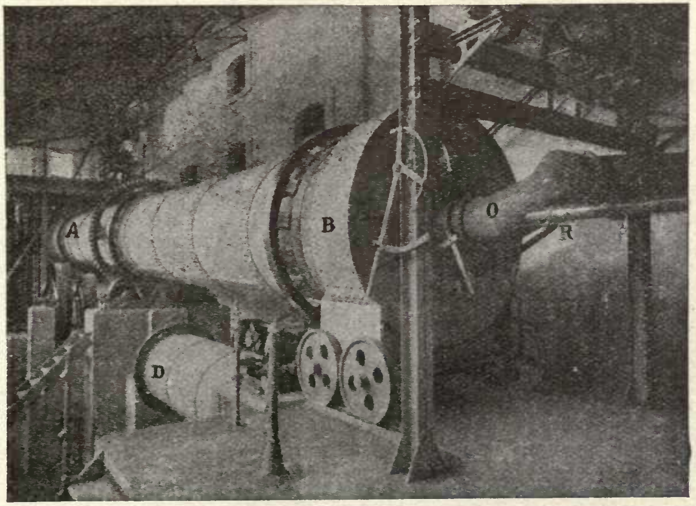


FIG. 304.

The fan is now placed by preference at the lower end of the cooling cylinder so that it blows in cool air at a slight pressure and the complicated and inconvenient cooling of the fan is not necessary. At the top of the cooler the air arrives similarly at a high temperature. The instantaneous combustion of the coal produces a very high temperature (1500° or above), but the refractory material which lines this part of the tube to a length of 4 to 5 metres (burning zone, *B*) is easily destroyed, and if the foreman does not regulate the heat carefully the cement may melt and agglomerate to a single mass which may finish by obstructing the furnace. These difficulties have recently been overcome by making the part of the kiln corresponding with the burning zone very large and thus increasing the capacity of this zone, and also the output of the kiln itself. The lower mouth of the kiln is closed by a large vertical cast-iron plate, *B*, covered internally by refractory material and carrying the large pipe for the hot air and the smaller pipe for the powdered coal. This plate is mounted on wheels in such a way that it may be brought to within a few millimetres of the furnace mouth, whilst leaving the furnace free to rotate.

The excess of hot air, which is not used for the combustion of the coal, is used for drying it before grinding.

The consumption of fuel in rotary kilns varies according as the material is used in paste form or as a moist powder, and may be from 22 to 30 kilos.[1] Low-grade coal may also be employed or even coal waste, because, being finely powdered, it burns even if it contains 10 to 15 per cent. of ash. The consumption of power to drive a large rotary kiln and the corresponding cooler is 20 to 25 h.p.

When the clinker is discharged from the cooler of a rotary kiln, it is gently sprayed with 1 to 2 per cent. of water, and may then be stored for grinding. This water saturates a portion of the calcium oxide and a cement which sets rather more slowly is thus obtained; in any case it acquires greater stability of volume, because the calcium oxide is slowly transformed into hydroxide and carbonate and undergoes no further alteration.

The cement from rotary kilns differs in general from that obtained in vertical kilns by its greater resistance to compression (*see below*, Cement Testing).

One of the great advantages of rotary kilns consists in the great saving of hand labour. One good fireman can supervise two rotary kilns. In a large works visited by the writer at Rudersdorf-Kalkberg, near Berlin, two complete plants of equal output were working side by side. One produced 240 tons of cement daily with 4 small rotary kilns and employed 35 workmen in all by day and 35 by night. The other produced 240 tons with 12 vertical kilns, and employed 98 workmen by day and 98 by night.

The Atlas Company in America alone possesses more than 140 rotary kilns, and in the United States there were about 1000 rotary kilns in 1910. In Europe at least 150 such plants have been erected of recent years. In Italy there are now three or four works using rotary kilns.

---

[1] The theoretical consumption of fuel for burning cement in fixed vertical kilns would be 9 kilos of coal per 100 kilos of burnt cement. In practice, the best kilns consume 13 to 14 kilos. In rotary kilns the theoretical consumption of fuel, according to Newberry, on working by the dry method (with a paste containing 8 to 10 per cent. of moisture) would be 17·5 to 20 per cent., according to the lesser or greater excess of air. The practical consumption in the best rotary kilns has to-day been reduced to 22 to 24 per cent., whilst a few years ago 30 to 32 per cent. was still employed. With a paste containing 35 to 40 per cent of water and assuming an excess of air for the combustion, the theoretical consumption of coal would be 25 to 26 per cent.; in practice in the best furnaces, 28 to 30 per cent. is consumed to-day, whilst formerly more than 40 per cent. was used.

Byron E. Eldred (1910) established the following theoretical thermal balance for the burning of cement. Taking the theoretical composition, $3Ca_3SiO_5 + Ca_2Al_2O_5$ with 68·55 per cent. of CaO, 20·10 of SiO_2 and 11·35 of Al_2O_3, to obtain 100 kilos of cement would require 122·32 kilos of calcium carbonate, 28·75 of clay and 6·7 of sand, a total of 157·77 kilos of mixture. To heat this to 900° (first phase: calcination) requires 34,596 Cals., to dry the clay 4882 Cals., and to dissociate the limestone 55,157 Cals., altogether 94,635 Cals. For the burning (second phase: formation of clinker at 900 to 1300°) 12,000 Cals. are necessary; since, however 4717 are produced by exothermic reactions, 7283 Cals. suffice. The clinker leaving the kiln hot carries with it 39,000 Cals. The fuel necessary (giving about 8000 Cals. per kilo) will be about 11·5 kilos for the first phase, about 1 kilo for the second phase, and 0·5 kilo for radiation losses: Total, 13 kilos of coal required theoretically per 100 kilos of cement. In practice, utilisation of 80 per cent. of the value of the coal in the first phase and 84 per cent. in the second phase is assumed, so that the fuel efficiency is about 67 per cent.; thus about 19 kilos of coal are required per 100 kilos of cement.

It has been calculated that the motive force required in a cement works corresponds with a daily consumption of coal equal to 3·5 to 4·5 per cent. of the weight of burnt cement, or according to the type of plant 1 h.p. will be required per 4 to 6 cwts. of cement per day.

Rotary kilns are built more especially by the firms of Polysius, Krupp, Smidth, Löhnert, Pfeiffer, etc.

GRINDING OF THE BURNT CEMENT (CLINKER). It is now generally admitted that the good qualities of Portland cement are dependent largely on the degree of fineness of the ground clinker. The best ground cements to-day leave a residue of less than 25 per cent. on a sieve of 4900 meshes per square centimetre, and this result has been obtained by using more perfect machinery, which has already been described in connection with the grinding of the prime materials.

In modern works the clinker is passed through ball mills, or preferably through kominor mills, and the product coarsely ground; the meal is then passed through the tube (Dana) mills, already described. Since the finished clinker is much harder than the limestone and clay or marl, these tube mills are lined with flint, and the crushing material also consists of flint pebbles.

Both in the grinding of the prime materials and in that of the burnt cement, the tube mills may be replaced by pneumatic separators of the Pfeiffer type, these (already illustrated) resulting in an economy of power. In either case sieves are now dispensed with.

In almost all cement works the finished product has of recent years been subjected to a very simple treatment in order to lengthen the time after which it will set when mixed with sand and water, namely, by mixing it, on introduction into the grinding plant, with 1 to 2 per cent. of natural gypsum in lumps.

This gypsum appears to combine in the presence of water with a portion of the calcium aluminate of the cement, thus lengthening the time of setting, which would occasion many difficulties if it were too short. For buildings cements containing more than 3 per cent. of gypsum are not accepted.

The more important works have a very good system of storing the cement after grinding before it is placed on the market, because if a small quantity of free quicklime is present, this is slowly hydrated and carbonated by the moisture and carbon dioxide of the air, and the resulting cement is more stable as judged by the test of deformation or of stability of volume.

For this reason the cement discharged from the grinding apparatus is carried by means of elevators or endless rubber bands to the upper portions of large warehouses, which sometimes have a capacity of thousands of tons, and is gradually discharged at the base after some months by means of helical transmitters, which correspond with the various charging doors, and thus it is filled, weighed, and the packages containing 50 kilos each automatically closed.

For foreign or oversea markets the cement is filled into barrels lined with paper, the nett weight being 170 kilos and the gross weight 180 kilos.

In America the use of paper sacks has been tried for transport to short distances, and these cost less than 1½*d.*

Other cement-forming substances, analogous to Portland cement, are, for example, the "grappier" cements prepared from the argillaceous residues from hydraulic cements (which do not crumble with water), these being corrected with clay and lime before burning. It is obvious that these cements are of inferior quality to Portland cement.

Of late years the utilisation of blast-furnace slag has acquired great importance for the preparation of *slag cement.* The annual production of blast-furnace slag is 50,000,000 tons. The composition of this slag varies within the following limits: SiO_2, 27 to 35 per cent.; $Al_2O_3 + Fe_2O_3$, 8 to 20 per cent.; CaO, 44 to 52 per cent.; MgO, 0·6 to 5 per cent.; H_2SO_4 (sulphates), 1·2 to 3 per cent.; those slags in which the ratio of CaO to SiO_2 is greater than 1 are most suitable. Cements of the true Portland characteristics are obtained from slags containing large amounts of silica and alumina by adding lime. Blast-furnace slags with a dolomitic basis do not serve for cement, the best slags containing about 36 per cent. SiO_2, 14 per cent. $Fe_2O_3 + Al_2O_3$, and 46 per cent. of lime, these being corrected with the calculated proportion of lime.

In 1861 the firm of Fr. Wilhelm, of Mülheim, attempted to use a cement made of slag only by modifying the fluxes in the blast furnace when necessary, but the results were not of practical value. The molten slag from the blast furnace is to-day obtained in a friable and easily ground condition by pouring it into water. A powder is thus obtained which is mixed with 30 to 40 per cent. of fat slaked lime or hydraulic lime and then burnt in the usual rotary kiln; the hot clinker is sprayed with water to slake the remaining free lime, but it is well to add 2 per cent. of gypsum to retard setting. Slag cements have a specific gravity of 2·7 to 2·8, and usually contain calcium sulphide (up to 4 per cent.), and they set in more than 10 hours. In the United States these cements are also called *pozzolana*, of which 20,000 tons were manufactured in 1906, about 600,000 tons in 1909, and 800,000 tons in 1910.

In England, Denmark, and Russia the sale of mixtures of slag cement with ordinary Portland cement is prohibited. Such prohibition was discussed in Germany before the European War, but frequent use is there made, under the name *ferro-cement*, of a mixture of 70 per cent. of Portland cement with 30 per cent. of slag cement; mixtures in which the slag predominates are termed *blast-furnace cements*.[1]

CEMENT RESISTANT TO SEA-WATER. According to Le Chatelier, Newberry, and Michaelis, such cement is obtained on replacing a large part of the clay by ferric oxide (ferrite cement). Cement blocks which have set in the air resist better than those formed in the sea-water itself.

Whereas in laboratory tests cement is injured by solutions of various salts, it is found in practice that good cement structures stand well in both sea-water and fresh water, especially the parts always immersed in the water, possibly because a protecting layer of salts or of impervious compounds forms on its surface. If a salt solution penetrates the interior of a cement block which then dries in the air, when the salts remaining crystallise out in the pores they promote cleavage or corrosion, but the same happens with any porous stone.

In France, whereas a cement with 3 per cent. of SO_3 is allowable for use in fresh water, only 1·5 per cent. of SO_3 (of gypsum) is permissible in the case of sea-water cement. This is not justified by practical experience, and at the Congress of the Union of German Portland Cement Manufacturers in 1912 the proposal was made to fix for cements in general (including those for salt water) a maximum limit of 2·5 per cent. SO_3.

A so-called *white Portland cement* has also been placed on the market, this being obtained by heating either a mixture of pure calcium carbonate with pure kaolin and about 3 per cent. of gypsum to 1200°, or a mixture of 100 parts or less of felspar, 100 parts of kaolin, about 30 parts of magnesite, and about 4 parts of sodium chloride to 1400° to 1500°. This cement is also used for statuary.

CEMENT TESTING. Portland cements form fine powders of a grey, greenish-yellow or reddish-yellow colour; they require 30 per cent. of water to convert them into pastes of normal consistency, whilst cements of other qualities require up to 45 per cent. of water, and hydraulic cements even more. In practice, the cements are used as a paste to which pure, fine sand is added in the proportions of 1–3 parts of sand, 1 part of cement, and 0·5–0·7 part of water.

The *absolute density* of Portland cement varies from 3·10 to 3·25, whilst that of other cements is lower than 3, and varies from 2·7 to 3, that of hydraulic cements being between 2·50 and 2·85. The specific gravity is determined with a pyknometer or with a graduated cylinder (*see* pp. 75 and 111), turpentine oil or preferably carbon tetrachloride being employed as the liquid, and the cement is used after passing through a sieve of 900 mesh (per square centimetre).

The *apparent density* is determined by the weight of one litre of powdered cement, collected and weighed with prescribed precautions in suitable vessels.

The *degree of fineness* is also of great practical importance. The best qualities yield a residue of less than 10 per cent. when they are passed through a sieve with 4900 meshes per square centimetre, and ordinary qualities less than 20 per cent. (or less than 3 per

---

[1] The percentage compositions of an ordinary blast-furnace slag and of various types of cements are as follows:

	$Al_2O_3,2CaO$	$SiO_2,2CaO$	SiO_2,CaO	CaO	Total cement constituents
Slag . . .	34·27	50·17	6·86	—	91·30
Slag cement . .	25·36	38·60	5·28	12·10	70·24
Portland cement .	25·49	53·79	—	12·32	79·28
Ferro-cement .	28·12	52·60	2·86	8·62	82·78

Thus, blast-furnace slag represents a species of Portland cement deficient in lime.

cent. with a sieve of 900 meshes per square centimetre). For this purpose the Tetmajer sieve (Fig. 305) is used, 100 grams of the cement being sieved until less than 0·1 gram passes through on giving 25 turns to the handle.

In valuing a cement it is necessary to take the *time of setting* into account. This is done by working the cement up to a paste with about 30 per cent. of water (at 15° to 18°, the quantity of water varying with the fineness) added all at one time, and stirring it with an iron spatula for 1 to 5 minutes. The paste is immediately placed in the mould, *a* (Fig. 306), 4 cm. high and 8 cm. in diameter, and setting is said to have commenced when the needle, *c* (Vicat's needle, with a weight of 300 grams and a point of 1 mm. cross-section), does not succeed in penetrating through the mass contained in the mould; setting is said to be finished when the same needle does not scratch it and does not even penetrate the surface of the block of cement in the mould.

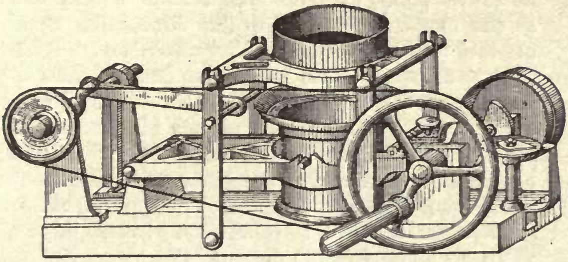


FIG. 305.

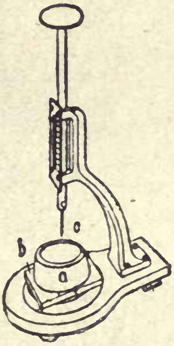


FIG. 306.

Rapid-setting cements are no longer scratched after 15 to 30 minutes, whilst slow setting cements require 5 to 10 hours, and hydraulic cements over 24 hours (excepting those which are strongly hydraulic).

The determination of the *resistance to compression and tension* is also important. The first is determined by submitting a brick of cubical shape and 50 sq. cm. cross-section to pressure in a hydraulic press, furnished with a mercury manometer. The brick is obtained by mixing 1 part of cement with 3 parts of *normal sand* (clean quartzose sand containing at least 90 per cent. of SiO_2, which should pass completely through a sieve with holes of 1·35 mm. diameter, and should all be retained by a sieve with holes of 0·77 mm. diameter) and about 8 per cent. by weight of water, and then compressing the whole with a mechanical hammer (*see below*), and exposing it to the air for 1 day and in water for 27 days before the test is made.

It may also be tested after 7 or more days, and the resistance is expressed in kilos of pressure per square centimetre of surface of the face exposed to the pressure until it crumbles or breaks. For good Portland cement, the resistance after 8 days varies between 180 and 190 kilos, and after 28 days between 200 and 220, whilst after 90 days it exceeds 250 kilos.

For these determinations Amsler and Laffon's hydraulic presses are used in many laboratories (Fig. 307), and with them pressures up to 600 kilos per square centimetre can be exerted on the little cube, 5, held down by the screw, 6, whilst the piston, 2, is lowered by the handle, 1, and transmits the pressure to the oil, which raises the piston of the bell, 10, the pressure being simultaneously transmitted below to mercury in a vessel communicating with the manometer, 9.

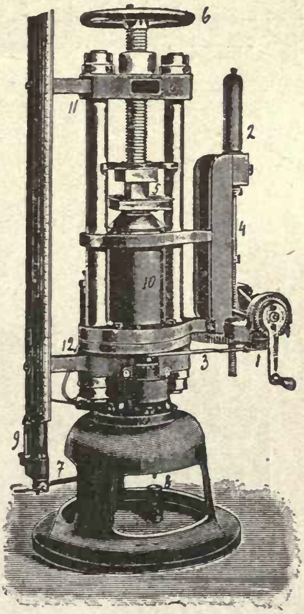


FIG. 307.

Resistance to tension is determined on a cement brick which, immediately after being made with water and sand, as above, is compressed in a dumb-bell-shaped mould (Fig. 308), of exactly prescribed dimensions, and compressed with a mechanical hammer (Fig. 309), which weighs 2 kilos and gives 150 blows. The tension test is made with the Frühling-Michaelis balance (Fig. 310), which has a ratio of 1 : 50 between the two arms. The cement brick to be tested, *a*, which has first been left in the air for 1 day and then in water for 27 days, is clasped by two pairs of pincers, *A*, and when equilibrium has been established, the pan, *B*, is suspended and the mouth of the reservoir *D* is opened so that the lead shot contained in it are allowed to fall into *B* until the test piece, *a*, breaks at the narrowest point, where its cross-section is 5 sq. cm.; at the moment of fracture the discharging mouth of the vessel *D* automatically closes, and all that is now necessary is to weigh the pan, *B*, with the lead shot. From this weight, multiplied by 50 and divided by 5 (number of square centimetres) or simply multiplied by 10, the resistance to tension is obtained, expressed in kilos per square centimetre. After lying in water for 7 days a normal cement shows a resistance of 16 to 20 kilos, after 28 days of 21 to 25 kilos, after 90 days of 25 to 32 kilos, and after 3 years of 36 to 38 kilos. In general the resistance to compression is 9 to 10 times greater than the resistance to tension during the first days, but after some time it is 12 to 16 times greater, although in rapidly-setting cements after 28 days in water the resistance to compression is slightly lower than during the first days.

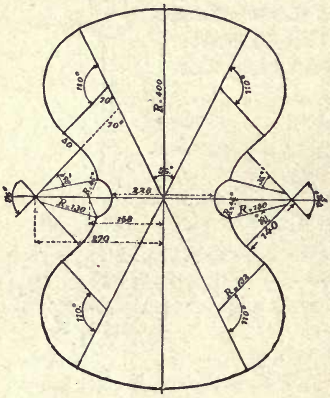


FIG. 308.

A most important property of cement is that of giving mortars *which do not swell.* This means that in the test in which the bricks are formed these must not show deformation, cracking, radial cleavage, or enlargement towards the edges after soaking in water for 28 days. Cakes of soft mortar prepared with the cement may be placed on a glass plate; the cake, 10 cm. in diameter and about 2 cm. thick in the centre, is allowed to stand in the air in a moist spot for 24 hours and then immersed in water at 15° to 20° and observed once a week, as described above. This is called the cold test, but the Michaelis hot test is now generally used, because it is more rapid and also enables a clear opinion of the quality of the cement to be obtained; it is usual to prepare a little cylinder

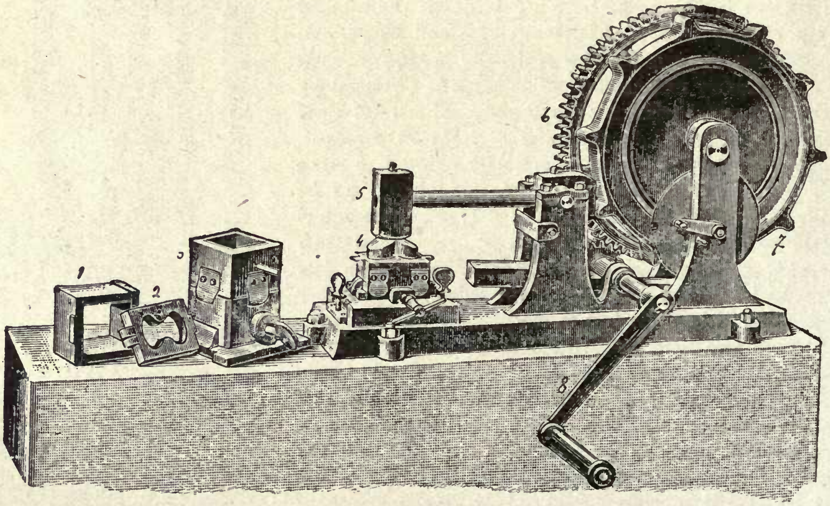


FIG. 309.

of mortar from the cement which is placed in Le Chatelier's ring (Fig. 311), which has a diameter of 3 cm. and is 3 cm. high, and is formed of a flexible metallic sheet split at one point where two long needles are fixed to it at right angles. These indicate the increase in volume of the cement cylinder on a quadrant, after the cake has been dried for 24 hours in the air, left in boiling water for 6 hours, and then cooled in ordinary water for 24 hours. The deformation and expansion are proportional to the distance which separates the two needle-points of the apparatus.[1] Defects of swelling or expansion may be caused by bad grinding and mixing, by insufficient burning (in which case much free lime remains), by excess of lime, of gypsum, or of magnesia; in fact, if during setting there is continuous formation of crystalline calcium hydroxide (due to excess of lime throughout the mass, it is not sufficiently resistant, and so much pressure is produced that it breaks to pieces. For similar reasons more than 2 per cent. of SO_3 in the form of

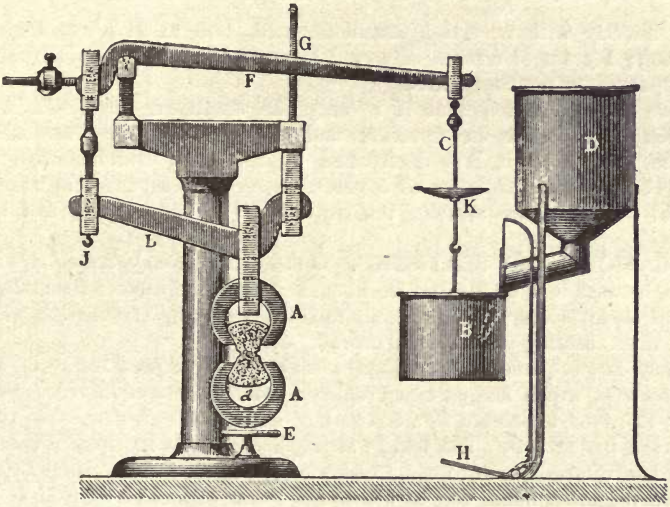


Fig. 310.

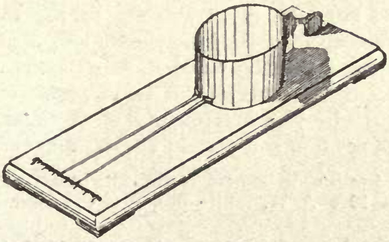


Fig. 311.

---

[1] The Michaelis hot test, which is sometimes carried out on simple spheres of the cement dried for 24 hours in the air and then boiled for 3 hours in water to ascertain if cracks form, does not give reliable results for certain cements which set slowly in the air, and there are also good cements yielding spheres which break down in boiling water. In such cases it would suffice to leave the cylinders or spheres to dry in the air for 48 hours, or to modify the test as follows (G. Hentschel, 1911): With normal mortar from the cement a cake is formed, this being placed for 15 minutes on a block of absorbent porous gypsum and then heated on a sheet of 2 mm. iron over direct flame until the water is completely evaporated; when cold, it is immersed in cold water for 10 minutes, and then allowed to harden in the air for 3 hours; finally it is left in boiling water for 3 hours and examined to ascertain if cracks have formed.

sulphates or 5 per cent. of magnesia (MgO) cannot be allowed in cement; a cement containing 1·5 per cent. of free lime is expansive, and this is corrected during manufacture by the addition of gypsum.[1]

An unadulterated cement should lose less than 2·6 per cent. on ignition, and the alkalinity produced in water with which 0·5 gram of the cement has been mixed should require 4 to 6·5 c.c. of $\frac{N}{10}$ hydrochloric acid for neutralisation. On treating 1 gram of cement directly with normal hydrochloric acid, 18·8 to 21·7 c.c. are required for neutralisation; 1 gram of cement dispersed in water should not reduce more than 2·8 mgrms. of potassium permanganate.

We have already stated that it is only the combined silica, and not the free silica, which is of value in cements, and therefore in the chemical control of cements the total silica is first determined by the usual methods, and the portion soluble on boiling in a solution of 5 per cent. sodium carbonate is then also determined; that portion which remains undissolved is free silica (sand) and is dried and weighed.[2]

APPLICATIONS AND STATISTICS. Cement has to-day acquired extraordinary importance, because it is used in all works under water or in moist localities, and is also used as *concrete* in prisms or large blocks formed by mixing the cement with sand and water and then allowing it to dry in the air.

Extremely large quantities are used to-day for structures made of *armoured* or *reinforced concrete*, which has partially replaced iron and wood for the construction of buildings. Reinforced concrete is a network of cast-steel bars and wires embedded in, and supported by, cement. The tensile strength of iron is 10 times greater than that of cement, and the resistance to compression of the latter is 10 times greater than that of iron. On the other hand, the coefficients of linear expansion of iron and of cement are almost equal, being 0·0000135 for cement, and 0·0000123 for iron, so that by using iron and cement together the advantages of both materials are united, and the disadvantages of either avoided, a constructive material being obtained which is relatively cheap and of great strength. Steel girders or wires do not rust when they are surrounded by the mortar, which consists of 1 part of cement and 3 parts of pure, washed sand, and the adhesion is extremely good. Entire buildings, from basement to roof, are to-day constructed of reinforced concrete, including the dividing walls and the flooring.

Cement is transported for long distances in wooden barrels lined with cardboard of 170 kilos net weight and 180 kilos gross weight. In the United States these weights are 127 and 135 kilos respectively. Half-barrels are also used. In small quantities and for immediate consumption it is despatched in small sacks containing 50 kilos, which must be kept in a dry spot. In America the use of paper sacks, which cost 1*d.* to 1·2*d.* each, has been recently tried. The best quality of Portland cement was sold in Italy in 1906–1907 at about £2 per ton, and cement of second quality at about £1 12*s.* per ton,

---

[1] The *determination of free lime* in cement is difficult, because neither water nor an aqueous solution can be used. In 1910 A. W. White proposed the following test, which is, however, qualitative only.

A few milligrams of the powdered cement are placed on a microscope slide and treated with a drop of a reagent consisting of a mixture of 5 grams of phenol, 5 grams of nitrobenzene, and 2 drops of water. The whole is then covered with a cover-slip and observed under the microscope by polarised light. If free lime or calcium hydroxide is present, small bundles of shining, needle-shaped crystals are seen in the dark field in a short time. Dolomite, calcined magnesia, and calcium silicate do not give such crystals.

In 1909 R. Brandenburg proposed a quantitative test by distilling a given weight of the cement with a solution of ammonium bromide in absolute alcohol and absorbing the ammonia which distils over in a given volume of normal sulphuric acid.

[2] In Italy it has been established by the Ministry by a decree of January 10, 1907, that for public works cement must satisfy the following requirements: Its volume must be constant by the hot and cold test; its absolute density must be not less than 3·05; the maximum residue on a 900-mesh sieve must be 2 per cent., and on a 4900-mesh sieve, 20 per cent; the setting of the mortar must not commence before 1 hour and must not finish before 5 hours or after 12 hours; the resistance to tension must be at least 16 kilos after standing in water for 7 days, and 20 kilos after 28 days. The resistance to compression on the seventh day must be 180 kilos and on the twenty-eighth day 220 kilos; the content of gypsum, expressed as SO_3, must be lower than 1·2 per cent., and the amount of magnesium oxide, MgO, must be less than 3 per cent.

but during the crisis of 1907 the price dropped to below £1 4*s.* The various qualities are distinguished by various coloured bands.[1]

The development of the cement industry in Italy is shown by the following figures (tons):

	1890	1900	1905	1910	1911	1912	1913	1914	1915	1916	1917
Production .	104,000	198,280	333,400	846,968	979,578	1,091,976	—	—	—	—	—
Imports .	—	—	14,900	20,656	22,086	20,891	49,736	12,800	510	640	6,217
Exports .	—	—	7,290	6,673	10,011	45,230	17,200	36,500	38,700	42,200	12,800
Price per ton	—	£2	£1 16*s.*	£1 8*s.*	£1 7*s.*	£1 8*s.*	£1 7*s.*	£1 5*s.*	—	—	—

During the European War, owing to the enormous cost and scarcity of coal, the price of cement in Italy rose to £4 16*s.* per ton in 1915, £7 4*s.* in 1916, £10 in 1917, and more than £12 in 1918.

The Italian production and consumption are mainly of slow-setting cement, which enjoys a protective duty of 10*s.* per ton, whilst quick-setting cement (with a duty of 4*s.* per ton) is mostly imported.

In Italy cement is sold in 50-kilo sacks closed with thread and sealed with lead, the colour (black, blue, or red) of the thread indicating the quality—1, 2, or 3—the last being the poorest.

United States. Up to 1882 only natural cement (260,000 tons), known as Rosendale (from argillaceous limestone rich in magnesia), was made, and in 1892 this preponderated, but in 1905 more artificial cement was made. In 1913 the Atlas Company, with four works, produced 6000 tons per day. The price reached a minimum of £1 4*s.* per ton in 1911.

---

[1] Production of **Cement** in different countries (thousands of tons):

Country		1892	1900	1905	1910	1911	1912	1913
United States .	production	800	2100	4250	8000	10,000	14,000	15,000
	exportation	—	—	115	135	500	700	500
	importation	—	—	400	86	8	11·6	14·3
Germany .	production	—	3400	4300	5900	—	—	—
	exportation	—	—	650	725·8	845·8	—	—
	importation	—	—	220	240	253	—	—
France . .	production	—	907	—	—	—	—	—
England .	production	1200	1300	1400	—	—	—	—
	exportation	—	670	770	753·8	—	—	—
Belgium .	production	180	—	660	—	—	—	—
	exportation	—	—	600	—	—	—	—
Finland .	production	—	—	—	—	400	—	—
	importation	—	—	—	—	100	—	—
Russia .	production	—	1100	—	—	—	1500	1750
	exportation	—	3·8	—	—	—	—	—
	importation	35	28	10	—	150	186	—
Denmark .	production	25	—	200	440	—	—	—
	exportation	—	—	55	—	—	—	—
	importation	23	—	18	—	—	—	—
Norway .	importation	—	—	—	50	—	—	—
Spain .	production	—	—	—	500	—	—	—
Rumania .	production	—	—	—	70	—	—	—
Japan .	production	—	—	100	300	—	—	—
Sweden .	exportation	—	18	35	—	—	—	—
Australia .	importation	—	—	40	—	—	—	—
China .	production	—	—	—	—	—	254	—
Canada .	production	—	—	—	500	—	—	—
Chili .	importation	—	—	95	—	—	—	—
Switzerland .	production	86	120	—	—	—	—	—
Argentine .	importation	—	—	—	300	—	—	—
Brazil .	importation	—	—	—	500	—	—	—
Egypt .	production	—	—	—	25	—	40	—
	importation	—	—	—	87·5	—	—	—
India .	importation	—	—	—	—	—	160	—

In 1911 there were working 115 cement works, with 916 rotary kilns; three-fourths of the kilns in America are fired with coal, one-fifth with mineral oil, and about one-tenth with natural gas.

Germany. In 1911 there were 135 cement works, eight being for ferro-cement and eight for slag cement. Three hundred and thirty-four were Schneider kilns, 272 Dietsch, 85 other basin kilns, 74 annular kilns (Hofmann type, p. 744), and 209 rotary tube kilns. A syndicate of all the German cement manufacturers was formed in 1914.

Spain produces cement mainly in the provinces of Barcelona and Guipuzcoa.

In *Denmark* a cement works (at Aalborg), placed conveniently near a bank of clay and friable limestone, and having easy water transport available, in 1912 produced cement at a cost of 11*s.* per ton.

In *Rumania* about 70,000 tons of cement, home-produced, were used in 1910.

Egypt imports cement (*see* Table), 40 per cent. from England, 36 per cent. from Belgium, 9 per cent. from France, and 7 per cent. from Germany, this being usually artificial cement, quoted at £1 16*s.* per ton at Alexandria. There are two works: an old one, producing 24,000 tons per annum and using local raw material (Mokattam), and another, erected in 1912, this using raw material from the Adriatic coast of Austria and being capable of an annual output of 15,000 tons.

The *Argentine* imported about 300,000 tons in 1910 (one-third from Belgium, one-fourth from England, one-fifth from France, and one-eighth from Germany), and then received only 260 tons from Italy, but in 1915 Italy sent 4540 tons. While the freight from England, France, and Belgium amounts to 11*s.* to 13*s.* 6*d.* per ton, that from Genoa costs 17*s.* 6*d.* In France and Germany the wooden cement barrel costs 1*s.* 1*d.* Before the war the price of Belgian cement was £1 12*s.* and that of English £2 per ton.

In *India* all the cement used up to 1912 was imported, especially from England, but also from Belgium and Germany, although the cost of transport from Germany amounts to 17*s.* 6*d.* to £1 per ton, in addition to 7*s.* for packing and an *ad valorem* import duty of 5 per cent., the total being about £1 5*s.* to £1 9*s.* per ton. Recently two large works have been erected at Dandot, near Salt Range, between the rivers Jhelum and Indus.

In the *United States* about £60,000,000 is invested as capital in a hundred cement works. In 1909 an unsuccessful attempt was made to form a trust of cement works with a capital of £40,000,000.

ULTRAMARINE

This is a compound which is found in nature in Persia and Turkestan under the name of *lapis lazuli*, and forms a hard mass of sp. gr. 2·75 to 2·95, of beautiful blue colour. It may be polished, and is then used as an ornamental stone. Its composition has not been clearly elucidated. It was obtained artificially by Gruelin in 1882 and is prepared to-day in large quantities by heating a mixture of about 100 parts of kaolin, containing less than 1 per cent. of Fe_2O_3, 46 parts of soda, 41 parts of sodium sulphate, 13 parts of sulphur free from arsenic, and 17 parts of coal, resin, or pitch in crucibles to a white heat for 40 hours out of contact with the air. Sodium sulphate may be used instead of soda, and thus there is both *sulphate ultramarine* and *soda ultramarine.* Reactions occur between the kaolin and the sodium sulphide produced by the interaction of the sulphate and the coal. According to Ger. Pat. 206,466 of 1907, the reaction may be completed in 5 hours by regulating the temperature to produce three phases, and by adding nitre or other oxidiser during the last phase.

Heating in crucibles is now replaced by the use of muffle furnaces in which flues and the muffle vault permit of uniformity of the temperature throughout the whole mass, and laterial apertures allow of the withdrawal of samples during the heating. The wet grinding, first carried out with stones, is now effected in tube mills, which give a sixfold yield. The action of the sulphur is accelerated if a little sodium hydroxide is added to the sodium carbonate.

The colour of ultramarine may be enhanced by treatment either with a little glycerine or with steam.

If the kaolin used contains more than 3 per cent. of water of hydration, this causes a loss of 5 to 10 per cent. of sulphur, which escapes up the chimney as H_2S, to the detriment of the neighbourhood. If green ultramarine is required instead of blue, the mass is heated to redness with 5 per cent. of sulphur in a muffle in a current of air, and the quantity of sodium in the ultramarine thus diminished. The crude ultramarine so formed is slowly cooled and boiled repeatedly with water in order to remove the excess of Na_2SO_4, Na_2CO_3, Na_2SO_3, etc.; the ultramarine is then separated in a hydro-extractor or a filter-press. It is mixed with 4 times its weight of magnesium carbonate, calcium carbonate, gypsum, or kaolin, and finely ground. The addition of a little glycerine renders the colour more intense. Products containing more SiO_2 may be violet or even red. By the action of HCl or HNO_3 vapours at 130° blue ultramarine becomes red.

Ultramarine contains sulphides and polysulphides, and thus with acids, or even with salts of an acid reaction such as alums, H_2S is evolved and decolorisation takes place, but the cause of the blue colour is not exactly understood.[1] It is insoluble in ordinary solvents. To the ultramarines containing most sulphur and silica, the formula, $Si_6Al_4Na_6S_4O_{20}$, is assigned, and it may be stated that no good ultramarine should contain more than 66 per cent. of silica and alumina ($SiO_2 + Al_2O_3$). The green, blue, violet, and red ultramarines are distinguished by their different proportions of sodium and sulphur.

The percentage composition of the various pure ultramarines of commerce varies between the following limits: Na, 17 to 21·5; Al, 16·1 to 16·6; Si, 17 to 18; S, 6·40 to 8·42; O, 38·40 to 41·30. *Boron ultramarine* contains 17 per cent. Na, 24 per cent. B, 1·2 per cent. S, and 58·7 per cent. O, and is obtained by heating in kilns (with or without air or water) a mixture of 3·6 kilos of $Na_2B_4O_7$, 1·5 kilo B_2O_3, and 0·9 kilo Na_2S; the blue colour appears when there are present in the molecule at least three B_2O_3 groups. Boron ultramarine is partly soluble in water.

A violet ultramarine also is known, part of the sodium being replaced by ammonia, but in contact with lime in paintings this decomposes with evolution of ammonia, whereas that prepared by Wunder in 1872, by heating it in presence of chlorine and then washing it, is very stable. In 1876, by the action on violet ultramarine of nitric acid vapour at 145° and then of hydrochloric acid vapour at 140° to 125°, a fine red ultramarine (*see* note) was obtained.

With acids blue ultramarine yields H_2S, but the violet variety (obtained from the first by elimination of one-sixth of the soda as NaCl) and the red do not yield H_2S and contain one-half their sulphur as thiosulphate.

In 1889 J. Wunder obtained a very deep blue ultramarine by boiling blue ultramarine with a solution of potassium carbonate, sulphide, or sulphate, about 30 per cent. of the sodium being then replaced by potassium.

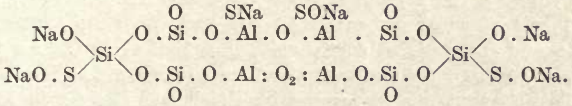
If ultramarine is heated in an autoclave at 180° with salt solutions, the whole or part of the sodium may be replaced by the metal of the salt (Ag, Li, K, $Hg^{\cdot}$, $Pb^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, Cd), the colour being less vivid; *e. g.*, cadmium ultramarine is yellow. The salts of trivalent metals (Fe, Cr, Al), on the other hand, decompose ultramarine, sometimes even in the cold, as is the case with alum (not owing to its acid reaction); in such case the filtrate

---

[1] Various reactions indicate that ultramarine is not an individual chemical compound, but rather a solid solution containing Al_2O_3, B_2O_3, SiO_2, oxides of sulphur (S_2O_3'' ion of the thiosulphates present), and possibly finely divided sulphur. The sodium thiosulphate, $Na_2S_2O_3$, is derived from the sulphite formed by oxidation of the sulphur, addition of sulphur occurring so that the ion SO_3'' becomes S_2O_3''. Green ultramarine (incomplete) containing sulphates turns blue when heated gently in the air with a little sulphur, since thiosulphate is thus formed. When ultramarine is heated for a long time in the air, its colour fades and ultimately disappears, and the same happens when it is heated in a current of hydrogen, H_2O and H_2S being then evolved at the expense of the S_2O_3 ions (J. Hofmann, 1910).

For the three ultramarines studied by him, J. Wunder gave the following constitutional formulæ:

(1) *Blue ultramarine*, $Si_6Al_4Na_6S_4O_{20}$, *i. e.*,



(2) *Violet ultramarine*, $Si_6Al_4Na_5S_4HO_{23}$, where the SNa of (1) is replaced by OH and the central SONa by NaS_2O_3.

(3) *Red ultramarine*, $Si_6Al_4Na_3S_4H_3O_{23}$, where the two lateral SONa groups of formula (2) become two SOH groups.

Some would attribute the blue coloration of ultramarine to a solid solution of sulphur, but such a hypothesis is contradicted by various facts.

contains soluble aluminium salt, whereas in cases where there is no decomposition the filtrate contains only sodium salts, and H_2S is not liberated in the autoclave. *Mercurous ultramarine* is greyish-blue, contains 57·27 per cent. Hg and 5·99 per cent. Na, and when heated loses all its mercury, the residue being a fine blue ultramarine, which turns yellow on heating, but becomes blue again in the cold, is resistant to acids, and is not completely decomposed even when boiled for 12 hours with *aqua regia.*

When heated in an autoclave at 180° with sulphur chloride or yellow phosphorus and CCl_4, ordinary blue ultramarine becomes white (leuco-base), and this reduction product gives the blue ultramarine immediately with alkaline hydrogen peroxide; the treatment with CCl_4 and P gives also phosgene: $CCl_4 + O = COCl_2 + Cl_2$, while with sulphur chloride SO_2 is evolved. With phosphorus trichloride a dirty red ultramarine is obtained, which assumes a fine blue colour when heated in the air. When heated to a red heat the red ultramarine becomes deep blue, but with acids this yields H_2S and differs from the ordinary blue form, since with HCl, Cl, and water vapour between 130° to 250° it does not change to red or violet, but remains blue; with mercurous nitrate at 180° it becomes deep blue, and in the hot loses all its mercury and becomes blue, but when heated it then remains blue and does not change to yellow (*see above*).

Ultramarine is used in painting in oil and water colours (in the Middle Ages natural ultramarine in powder cost up to £120 per kilo), for tinting and printing wallpaper, tapestry, etc., and it is also much used for correcting the yellowish shade of linen, starch, sugar, paper, etc.; it is used also in printing inks, in chromo-lithography, etc.

Whilst ultramarine cost 12*s.* 10*d.* per kilo in 1862, the price to-day is less than 9½*d.*, although the finer qualities have sold during recent years at 1*s.* 7*d.* to 2*s.* 5*d.* per kilo. The European production was 8400 tons in 1872, of which two-thirds was produced in Germany, but the production is not increasing to-day, because of the many substitutes having the advantage of being more resistant to the action of acids. Nevertheless, Germany exported 4840 tons of ultramarine in 1905, at a price of £25 12*s.* per ton, and 3770 tons in 1910, when 7000 tons were produced. France produces about 3000 tons per annum, and exported 2068 tons in 1913, 1441 in 1914, and 1248 in 1915. Austria-Hungary exported 965 tons and imported 90 tons in 1909. In Italy the consumption is about 600 tons per annum, and the works at Cogoleto (Genoa), now closed, had a capacity of 120 tons.

GALLIUM: Ga, 69.9; INDIUM: In, 1148; THALLIUM: Tl, 204

These are three rare elements which have much similarity with one another and with aluminium. Their basic character increases with rise of the atomic weight. Thallium also forms a lower oxide in which it behaves as a monovalent element, and yields a strongly basic hydroxide, TlOH. The specific gravity and boiling-point rise with increase of the atomic weight.

Before **GALLIUM** was discovered spectroscopically in a blende by Boisbaudran (in 1875) by means of two violet lines, its existence had been predicted theoretically in 1869 by Mendeléev, by means of his periodic system of the elements, and had already been called *eka-aluminium* by him. It is a white, tough metal which may be cut with a knife; it melts at 30°, and has a specific gravity of 5·9. It does not react with water and is only slightly attacked by HNO_3, but dissolves in HCl and in alkalis. With aluminium it forms liquid alloys which easily decompose water.

The **Chloride, $GaCl_3$,** the **Hydroxide, $Ga(OH)_3$,** and the **Sulphate, $Ga_2(SO_4)_3$,** have similar chemical and physical properties to the corresponding aluminium salts. The sulphide is white and insoluble in acetic acid, like that of zinc. An **Oxide, Ga_2O_3,** a **Chloride, $GaCl_2$,** a **Nitrate** and a **Gallium alum** are also known, besides other compounds.

INDIUM. This element was discovered by Reich and Richter in 1863 by means of its spectrum, which contains two pronounced blue lines. It is found in certain zinc blendes. It is a softer metal than lead, white, has a sp. gr. 7·4 and melting-point 154·5°; it does not alter in the air and burns with a blue flame, forming an **Oxide, In_2O_3.** It dissolves more rapidly in HNO_3 than in HCl or H_2SO_4. The **Chloride, $InCl_3$,** does not form HCl with hot water, thus differing from those of Al, Mg, etc. The **Hydroxide,**

$In(OH)_3$, is insoluble in alkalis, and the sulphate forms **Alums**. The **Chlorides**, $InCl_2$ and InCl, are also known.

THALLIUM. This is a somewhat less rare metal than the two preceding, and was discovered by means of its spectrum (which shows a fine green line) by Crookes in 1861, and by Lamy in 1862 in the sludge of the lead chambers, being contained in certain pyrites and blendes (and also in the sylvine and carnallite of Stassfurt). It is a metal which is rather less soft than sodium, and is separated from the above products by dissolving in H_2SO_4, and reprecipitating with HI in the form of TlI. The metal is of a leaden colour, of sp. gr. 11·8, melts at 302°, and boils at above 1600°. It is somewhat oxidised in the air, but remains unaltered under water. It is soluble in H_2SO_4 and in HNO_3, but is only slightly soluble in HCl, as it becomes covered by insoluble chloride. It burns with a bright green flame.

Thallium when acting as a monovalent element forms *thallous* compounds, which are similar to those of the alkali metals. Thus the hydroxide and the carbonate show an alkaline reaction and form salts similar to those of potassium, with which they are isomorphous; also thallous sulphate forms an alum, etc. As a trivalent element, thallium forms *thallic* compounds, which have a certain similarity with those of aluminium, but thallic sulphate forms an alum containing 8 molecules of water of crystallisation instead of 24.

The halogen compounds of thallium are very insoluble, and in this respect the metal resembles silver. Glass containing thallium is now produced and refracts light very strongly, like lead glass.

ELEMENTS OF THE RARE EARTHS

This group comprises numerous more or less rare elements, not all of which have been sufficiently studied to make it certain that they are true elements. The better known are: **Scandium, Sc,** 44·1; **Yttrium, Y,** 89; **Lanthanum, La,** 139; **Cerium, Ce,** 140·25; **Praseodymium, Pr,** 140·6; **Neodymium, Nd,** 144·3; **Samarium, Sa,** 150·4; **Gadolinium, Gd,** 157·3; **Terbium, Tb,** 159·2; **Erbium, Er,** 167·4; **Thulium, Tu,** 168·5; **Ytterbium, Yb,** 172.

These elements are often found together with the rare oxides of thorium, etc., which have already been described on p. 504, and are extracted from the minerals there mentioned and separated from one another by complicated methods which utilise certain special properties of their salts, as in the case of the earths already described (p. 506).[1]

SCANDIUM. Mendeléev had already predicted the existence of this element before it was discovered, and had called it *ekaboron*, on account of its position as a neighbour to boron in the periodic system. It is obtained from wolframite and from tin slag; the purification, especially the removal of thorium, is long and difficult. The hydroxide, $Sc(OH)_3$, is obtained in a gelatinous form by the action of alkalis, and is insoluble in excess of the latter.

CERIUM is found in *cerite*, $Ce_4Si_3O_{15}H_6$, which contains 60 per cent. of this element. It has an appearance similar to that of iron, but does not alter in the air, although it burns at high temperatures. It is obtained also from the residues left after working up thorium (*see* pp. 504–506); in these it occurs as oxalate, which is calcined at about 800°, the residue being used for making cerium salts. Metallic cerium is obtained by electrolysis of the chloride, and it then contains only 2 per cent. of impurities (oxides and carbides), which are expelled by amalgamation of the cerium. Its sp. gr. is 6·92 at 25°, and it melts at 635°. It is ductile and malleable and may be obtained in leaves 0·015 mm. in thickness. The specific electrical resistance of cerium containing 4·5 per cent. Fe is

---

[1] Some idea of the importance of the rare earths, especially of compounds of cerium, thorium, etc., is obtained by consideration of the very varied uses to which they are nowadays put: in the manufacture of coloured porcelain, glass, and enamel to obviate the devitrification of fused quartz; the lining of furnaces; as electrical insulators, as abrasives, as a substitute for diamond in glass-cutting, as pigments, as anti-rust pigments, as dryers for oils (cerium), for colouring with metal salts, as mordants for aniline black, for weighting silk, for bleaching wool, for tanning and colouring hides, for photographic purposes, for the electrolytic oxidation of organic substances (cerium salts), as catalysts in the manufacture of H_2SO_4, HCl, Cl, and NH_3 (from the elements and from NH_4Cl), in the synthesis of quinoline (Skraup), for halogenation, for gas lighters, for purifying acetylene, for various medicinal purposes, for incandescent mantles, for pyrophoric metals, for reducing metallic oxides, for photographic lamps and pyrotechnics, for electric lamp filaments, in the special steels industry, etc., etc.

71·6 microhms per cu. cm. The pure metal is feebly paramagnetic. The specific heat between 20° and 100° is 0·0524; the thermal conductivity is high and the tensile strength is 9 kilos per sq. mm. The heat of oxidation is 1740 cals. per gram.

With boiling water it slowly evolves hydrogen and blackens, whilst with dilute and concentrated acids and with H_2O_2 (30 per cent.) large volumes of gas are liberated. In an atmosphere of chlorine it burns at 215° with a bright light and formation of the chloride; in the air it burns at 160° with a vivid light, in an atmosphere of hydrogen at 345° it forms the hydride, and with nitrogen at 1000° it yields a little nitride without development of light. It reduces CO_2 and CO to carbon. It forms alloys with many different metals. Pure cerium costs twice as much as gold. A highly endothermic pyrophoric alloy is obtained from 17 per cent. Mg and 83 per cent. Ce.

Cerium is now little used in the manufacture of incandescent mantles (*see* p. 505), and since the working of monazite sand (in Europe more than 2500 tons annually, containing 50 per cent. of cerium oxide) large quantities of cerium residues may be obtained cheaply (up to 1*s.* per kilo).

Cerium forms two series of compounds, *cerous* (Ce''') and *ceric* (Ce''''), and mention may be made of: *cerous chloride*, $CeCl_3$, which is colourless and readily soluble in water and alcohol and is obtained in various ways, *e. g.*, by heating the oxide in a current of chlorine; numerous double chlorides (*e. g.*, $CeCl_3$, $PtCl_4$, $13H_2O$); *cerous hydroxide*, $Ce(OH)_3$, obtained as a jelly from a cerous salt and alkali, and readily oxidised in the air, being coloured reddish and then yellow (*ceric hydroxide*); *cerous sulphide*, Ce_2S_3, formed by heating the anhydrous sulphate to dull redness in a current of H_2S, is cinnabar red to black; the *nitride, hydrazide*, and *carbide*, CeC_2, are known.

Of interest are the more or less hydrated *cerous sulphates*, $Ce_2(SO_4)_3 + 4, 5, 8, 9$, and 12 H_2O, which at 400° yield the anhydrous sulphate, which is very readily soluble in water at 0° (40 to 60 per cent.). There are various double sulphates, *e. g.*, $CeSO_4$, $3K_2SO_4$, and $Ce_2(SO_4)_3$, $(NH_4)_2SO_4$, $8H_2O$; *cerous nitrate* and the corresponding double salts (*e. g.*, $Ce(NO_3)_3$, $2KNO_3$, $2H_2O$), the *carbonates* and the corresponding double salts, etc. *Ceric salts:* the *hydroxide*, $Ce(OH)_4$, is yellowish (*see above*) and dissolves in nitric and sulphuric acids with red coloration, and yields the cerous salt with HCl. The *oxide*, CeO_2, obtained by heating to redness any cerium salt, is almost white in the cold and yellow in the hot, but traces of didymium are sufficient to colour it reddish; it is insoluble in HCl and in HNO_3, but dissolves in presence of a reducing agent (*e. g.*, HI); its heat of formation is 56·1 cals. (per $\frac{1}{4}$-mol., *i. e.*, an equivalent), so that cerium may be set free by Al (*see below*, lanthanum); when reduced by H at a high temperature it yields an unstable, deep blue oxide (perhaps Ce_4O_7), and a *para-oxide*, $(CeO_2)_{40}$, insoluble in alkalies, is known. Of some importance are the *ceric sulphates*, namely, anhydrous, $Ce(SO_4)_2$ (formed by heating the oxide with concentrated sulphuric acid, without solution occurring; it is yellow, and dissolves in water with a brownish-yellow coloration), the *hydrated sulphates*, $Ce(SO_4)_2{,}4H_2O$ (obtained by means of dilute sulphuric acid, with an orange-red solution), and the *double sulphates*, *e. g.*, $Ce(SO_4)_2{,}2K_2SO_4{,}2H_2O$, these being orange-yellow and very slightly soluble in water. Cerium *nitrates* and the corresponding double salts are red, *e. g.*, $(NH_4)_2Ce(NO_3)_6$, which is soluble in water, but only slightly so in nitric acid.

Pure ceric oxide costs £18 per kilo, the commercial product 12*s.*, pure cerous chloride £6 8*s.*, the crude chloride 7*s.*, pure cerous nitrate £2, and the crude nitrate 8*s.* per kilo.

LANTHANUM is found together with the rare earths in lanthanite (a carbonate of lanthanum and didymium) found in Bethlehem (Pennsylvania). It is a trivalent element (*see* p. 506).

It has a white metallic appearance, is ductile and malleable, and has the density 6·1; it decomposes water in the cold, oxidises easily in the air and burns with a bright flame, producing a white powdery *lanthanum oxide*, La_2O_3 (heat of combustion 1602 cals. per 1 gram La). Black *lanthanum nitride*, LaN, is formed when pure La is heated in a current of nitrogen. Dissolution of the oxide in acids yields the various *lanthanum salts*, which are colourless and astringent. With alkali hydroxide or carbonate, solutions of the salts give gelatinous *lanthanum hydroxide*, $La(OH)_3$, which is soluble in water (also obtainable by dissolving the oxide in water, this giving a large amount of heat), but insoluble in excess of alkali, has a slight acid reaction towards litmus, but easily fixes CO_2 and expels NH_3 from ammonium salts.

Lanthanum oxide is obtained in an impure state from cerite; its heat of formation is greater than that of alumina (74·1 cals. for an equivalent, *i. e.*, $\frac{1}{6}$-La_2O_3, as against 64·3 for Al_2O_3), but less than that of magnesium oxide, so that lanthanum can be liberated from its oxide by heating with magnesium powder, but not with aluminium powder. Of its compounds mention may be made of the *bromide; chloride*, $LaCl_3$, which gives many double salts (*e. g.*, $LaCl_3$, $PtCl_4$, $13H_2O$; $2LaCl_3$, $3PtCl_2$, $18H_2O$, etc.); *peroxide*, $LaO(OH)_3$; *sulphide*, La_2S_3, which is yellow; *azoimide*, $La(N_3)_2OH,1\frac{1}{2}H_2O$, which is colourless and explosive and is obtained by dissolving the hydroxide in hydrazoic acid (p. 376); anhydrous *sulphate*, $La_2(SO_4)_3$, and its various hydrates (9 and 16 H_2O), which are mostly slightly soluble and are less soluble in the hot than in the cold; *nitrate; phosphate; pyrophosphate; carbonate*, $La_2(CO_3)_3$, more or less hydrated (1, 3, $8H_2O$); *acetate*, which is coloured blue by iodine, like starch, and is an oxidising catalyst (it accelerates the oxidation of hydroquinone, for instance); the *oxalate* is more soluble than oxalates of the other rare earths.

Lanthanum costs as much as 16*s*. per gram, and the *nitrate* £12 per kilo (used for incandescent gas mantles).

PRASEODYMIUM and **NEODYMIUM.** These were at one time believed to form a single element, **Didymium**, which was later separated into the two others by Auer. Neodymium salts are red, whilst those of praseodymium are green, and the two elements also show different spectra.

YTTERBIUM. This is obtained from the earth erbia, which consists mainly of the oxide, Yb_2O_3, and is formed from *Gadolinite*, $(Gl_2Fe)(YbO)_2(SiO_4)_2$. Its salts give no emission spectrum and are colourless. In 1908–1909 Auer showed that ytterbium is formed of two elements, **Cassiopeium** and **Aldebaranium.**

YTTRIUM is found in *Gadolinite*, *Yttrialite*, etc., and may be separated from the cerite earths by means of the solubility of its double potassium sulphate in concentrated sulphuric acid. The oxide, Y_2O_3, is present in the filament of the Nernst lamp (p. 671).

SAMARIUM. This element is found in monazite. An oxide, Sa_2O_3, and a well-crystallised chloride, $SaCl_3$, are known.

FOURTH GROUP: TETRAVALENT METALS

GERMANIUM: Ge, 72.5; TIN: Sn, 119; LEAD: Pb, 207.1

These elements also form oxides of the type MeO in which they are divalent and which have a basic character increasing with rise of the atomic weight. The derivatives of the dioxides, in which the metals are tetravalent, have a weakly acid character which diminishes with rise of the atomic weight. Thus, such derivatives of lead are immediately decomposed by water. These elements have a certain similarity with silicon and carbon, although their character is more metallic.

GERMANIUM: Ge, 72.5

Mendeléev had predicted this element in 1871 and called it *ekasilicon*, also predicting its physical and chemical properties. It was discovered in 1886 by Winkler in the mineral, *Argyrodite*, which is a sulphide of silver and germanium, $GeS_2,3Ag_2S$, when all the predictions of Mendeléev were fully and exactly verified. He obtained the free metal by heating this mineral with carbon in a current of hydrogen. It is a very rare element, which has a white metallic lustre, gives a characteristic spectrum, crystallises in octahedra of sp. gr. 5·472, and melts at 900°. It is stable in the air, is insoluble in HCl (like silicon), and forms a hydroxide with nitric acid (like tin); it dissolves in molten alkalis. The derivatives of the oxide, GeO, which are called *germanous* compounds, are unstable, and those of the oxide, GeO_2, are called *germanic* compounds, and are characterised by their greater stability.

GERMANOUS OXIDE : GeO. This is obtained from the hydroxide which is formed by adding potassium hydroxide to germanous chloride.

GERMANIC OXIDE : GeO_2. This is formed from germanium with HNO_3, or by roasting the sulphide or hydroxide. It separates as a white powder, stable on heating. It is insoluble in acids, slightly soluble in water with acid reaction, and forms salts with bases.

GERMANIC SULPHIDE : GeS_2. This compound is obtained as a white precipitate from a hydrochloric acid solution of GeO_2 with H_2S; it evolves H_2S in the air and dissolves in alkali sulphides and in alkalis forming sulpho-salts.

TIN: Sn, 119

Tin is a metal which has been known to man since remote antiquity. It abounds in the form of oxide (*cassiterite, tinstone*, SnO_2) in certain deposits in Cornwall, Saxony, Peru, Tuscany, the island of Banka, etc., the largest tin works existing to-day being in the island of Pulo Brani, near Singapore.

The extraction of tin from cassiterite is relatively simple. The mineral is first crushed, levigated with water in order to separate it from much gangue, and is then roasted in a furnace with a revolving hearth. In this way the sulphur and arsenic are eliminated. After this the residue is again levigated and in certain cases is also treated with crude HCl in order to separate Fe, Cu, and Bi. Finally it is mixed with coal and completely reduced in a cupola or reverberatory furnace.

The tin drops to the bottom into a separate vessel. The slag which remains is again treated in a reverberatory furnace. The refining of the tin is carried out by melting it at a fairly low temperature in such a way that the impurities collect, together with foreign metals, into easily separable lumps. The tin thus purified is again melted and is continuously stirred with rods of fresh wood as in the refining of copper (p. 696), in such a manner that the oxidisable metals separate at the surface and pure tin remains.

The recovery of tin from scrap or turnings of tinplate (tinned sheet-iron containing 2·5 to 5 per cent. of tin) is an important question. At one time these turnings were simply heated and the molten tin collected, but it is preferable to treat them with hydrochloric acid or a mixture of $HCl + HNO_3$, slightly dilute and in the cold; thus 10 parts of crude HCl, 1 part of crude HNO_3, and 10 parts of water may be used per 100 parts of tinplate. From the solution so obtained the tin is precipitated by zinc foil after it has been almost neutralised. Of late years the electrolytic process has acquired importance in various modifications. According to the process of Siemens and Halske, the bundle of tinplate scrap is used as the anode in a bath of sulphuric acid (1 vol. of 60 per cent. acid + 9 vols. of water), in which 1 per cent. of free acid must always be present during electrolysis; spongy tin thus collects at the cathode, which consists of a tinned copper plate. A current of 100 amps. per square metre is used.

Better results are obtained by electrolysis in a hot bath at 70° to 80°, containing 10 per cent. of sodium hydroxide and 10 per cent. of NaCl, as proposed by Keith in 1876 (U.S. Pat. 176,658). In this way any varnish and grease on the scrap are removed.[1] The scrap is compressed into bundles and used as the anode, the cathode being formed of sheet iron, on which the tin separates. At the anode electrolytic oxygen is formed which, in presence of NaOH, forms sodium stannate with the tin dissolving in the hot solution:

$$Sn + O_2 + 2NaOH = SnO_3Na_2 + H_2O.$$

At the cathode electrolytic hydrogen is formed, and reduces the stannate, separating spongy tin and regenerating the sodium hydroxide:

$$SnO_3Na_2 + 4H = H_2O + 2NaOH + Sn.$$

The scrap iron which remains may be used in open-hearth furnaces for the preparation of

---

[1] The scrap is cleaned with hot 3 per cent. caustic soda solution for 5 to 15 minutes, the gum and solder being expelled by heating to 400° to 500°.

steel if it contains less than about 0·08 per cent. of tin. It is necessary to work at a low tension with a potential difference between the one bath and the other not greater than 2 to 3 volts, and a current density not greater than 0·75 amp. per square decimetre of cathode surface. L. Annoni in 1909 increased the surface of the cathode in order to obtain less difference between the extent of the anodic surface, which is formed of bundles of tinplate, and that of the cathodic surface, by forming the latter of iron wire netting. There should not be more than 5 per cent. of sodium stannate or more than 3 per cent. of sodium carbonate in the bath. The bath should be in continuous circulation from one vessel to the other so that the stannate may not be dissociated and may not be transported to the cathode by the current. It is also necessary to heat the bath in order to maintain it at constant temperature. The tin is removed every 12 hours by carefully removing the cathode with the adherent grey and spongy tin, immediately immersing it in a vessel of water and detaching the tin with a small scraper whilst it is immersed in order to avoid oxidation, which easily occurs. It is then rapidly and repeatedly washed and compressed into blocks which still contain 10 to 15 per cent. of water. These are melted in graphite crucibles, the surface being sprinkled with a little colophony in order to avoid oxidation. The slag and the tin residues are resmelted with coal in a reverberatory furnace. Tin from detinning works containing 89 to 99 per cent. of Sn is not suitable for the preparation of fresh tinplate, but is satisfactory for other purposes. In order to maintain the composition of the electrolyte constant it is necessary continually to replace a portion, and the tin is regenerated from the portions which are removed by saturating them with CO_2, and thus precipitating H_2SnO_3, which is sold to enamel works.

Another process which appears to give better results than the electrolytic process is the chlorination process proposed by Higgins in 1854 (Eng. Pat. 767) and perfected by Parmelee in 1870, Lambotte in 1884 (Ger. Pat. 32,517), and still further in 1905 by Th. Goldschmidt (Ger. Pats. 176,457, 181,876, and 188,018), who compresses the scrap into compact bundles, perforates them in all directions, washes them with a solution of hot sodium hydroxide and then with water, dries them, and heats them until the lead solder is melted. He finally brings them into contact with dry chlorine in cooled vessels under pressure. Pure stannic chloride collects below and pure iron remains, which is not attacked if the scrap and the chlorine are dry.

Traces of $FeCl_3$ easily cause the iron to rust, and this is avoided by subjecting it to mild electrolysis.

In 1909 about 160,000 tons of tinplate scrap were treated throughout the world, about 4000 tons of tin being recovered.

The Goldschmidt Company in Germany (Essen-Ruhr) treated about 50,000 tons of tinplate in 1908–1909 and quite 90,000 tons in 1911. With the Americans the Goldschmidt Company formed a trust with a capital of £600,000 to monopolise and treat tinplate scrap by the chlorine detinning process. Old tinplate of poor quality gives about 10 kilos of tin per ton, new scrap yielding 20 kilos or more. In Italy new scrap was sold before the European War at £4 per ton, used material at £1 4*s.* to £1 12*s.*, and the residual detinned iron at £2 8*s.* per ton.

PROPERTIES. Tin is a metal of silvery appearance which melts at 232° and distils at about 1500°. It has a specific gravity of 7·29. At the ordinary temperature it is pliable and malleable, and may be converted into extremely thin foil (tin foil), whilst at 200° it is brittle. It has a crystalline structure, and on bending sticks of tin the so-called *cry* of tin, due to the friction of the crystalline particles, is heard. On pouring HCl on to a surface of tin, radiating crystalline markings remain which give the metal a frosted metallic appearance. At a temperature of — 40° its structure is modified and powdery **Grey Tin** is obtained of sp. gr. 5·8. It is not altered in the air or by water. If kept fused for some time it becomes covered with a grey layer of tin oxide. It is soluble in cold, dilute nitric acid, in HCl, in concentrated H_2SO_4, and in hot NaOH, with evolution of H. With concentrated HNO_3, however, it forms metastannic acid directly without dissolving. It resists alkalis and weak acids, such as acetic acid and the other organic acids, very well in the cold.

Tin forms two series of derivatives, *stannous* compounds, in which it behaves as a divalent element, and *stannic* compounds, in which it is tetravalent.

On account of its resistance to ordinary reagents, tin is much used for objects and vessels in common use, and for tinning copper and iron utensils (kitchen utensils, etc.)[1]; tinplate, which consists of tinned iron, is obtained by immersing iron plates previously washed with HCl or H_2SO_4 in baths of molten tin. Tin foil is used for mirrors and for wrapping up foodstuffs. Much tin is used alloyed with other metals. Ordinary *solder* contains tin and lead in almost equal proportions and melts at a lower temperature than either of its components.

Bronzes contain tin and copper (*see* p. 699). *A tin amalgam* is also prepared for silvering mirrors.

The *world's production* of tin was 40,000 tons in 1880, that for subsequent years being shown in the table : [2]

---

[1] The firm of Postler & Co., of Dresden, placed a paste on the market in 1908 (*Löt-Blitz*) which, when stirred up with water, is spread on to well-cleaned metallic parts without dismounting them; the object is then heated directly with a benzine lamp, and a homogeneous tin surface is thus obtained directly.

[2] *World's Production of* Tin (tons):

Year	Germany	Malacca	Banca and Billiton	Bolivia	Australia	England	China	France	Total for World
1900	2,000	45,630	17,900	—	3400	4,336	—	—	—
1901	1,450	53,844	19,676	9,825	3399	4,639	3075	—	94,458
1902	3,000	54,575	19,178	10,313	3250	4,462	3850	—	95,628
1903	5,000	56,223	19,020	9,785	5013	4,351	2482	—	96,874
1904	5,000	61,655	14,812	13,186	4924	4,198	3027	—	101,802
1905	5,250	59,261	12,876	14,474	5109	4,540	4535	—	100,875
1906	7,400	59,373	11,435	16,657	6586	4,595	4011	—	102,657
1907	5,850	56,592	13,707	15,844	6718	4,478	3536	—	100,795
1908	6,400	63,685	13,986	17,305	5840	5,133	4631	—	110,580
1909	8,990	61,543	14,442	18,412	5470	5,281	4516	—	109,664
1910	11,394	57,637	14,478	18,517	4636	5,903	4572	—	105,743
1911	12,426	57,944	17,400	400	5150	18,800 *	6050	500	118,700
1912	11,000	61,528	18,350	500	5130	18,938 *	8782	500	124,700
1913	11,500	65,640	17,400	300	4870	22,000 *	6000	1200	128,900

* Including that from imported ore.

Bolivia is now of no importance as a producer of tin, but it has a growing output of tin ore, which is exported to England and Germany (the ores contain on an average 60 per cent. Sn). The ore is extracted mainly in four districts (La Paz, Oruro, Chorolque, and Potosi), some as much as 4500 metres above sea-level. The industry might assume a still greater magnitude if grave difficulties were not caused by lack of roads and railroads.

England produced Cornish ore amounting to 8290 tons in 1909, 7570 in 1910, 8355 in 1913, and 8085 (£640,000) in 1914, *i. e.*, about one-third of that imported. The imports of ore were 24,000 tons in 1909 and 26,000 (£1,800,000) in 1910.

England also imports and exports considerable quantities of more or less refined tin (98 to 99·8 per cent.):

	Imports tons	Exports tons
1909	41,725 (£5,600,000)	—
1910	46,285 (£7,160,000)	43,920
1911	45,906	45,576
1913	45,682	41,731
1914	40,691	44,209
1915	38,986	37,506

Germany also works up much Bolivian ore.

Italy imports all the tin it needs (in 1905 14 tons were produced from scrap). In 1905 the imports of tin and its alloys (with Pb and Sb) were 2300 tons, in 1906 3361, in 1909 2754 (£360,000), in 1910 2989, in 1911 2733, in 1912 2630, in 1913 3100, in 1914 2746, in 1915 4246, in 1916 2917, and in 1917 3254 tons (£840,000).

The production of tin in the *United States* began only in 1910 (at El Paso, Texas).

The *price of tin* varies greatly on account of speculative operations. In 1880 it cost £88 5*s.* per ton; in 1895 £66 per ton; in 1902 £120 per ton, and in 1906 up to £152 to £160, in 1908 £132, and in 1910 £156. During the European War the price rose to £580 (in London, July 1917), while in Italy as much as £1400 was paid.

The production of *tinplate* in the United States in 1891 was only 999 tons, and in 1904 rose to 458,000 tons, without including 65,000 tons imported from England, which produced 600,000 tons in 1908.

Italy produced 28,277 tons of tinplate in 1908, of the value of £517,538, and imported 14,000 tons of tinned, coppered, or oxidised iron sheet in 1909, of the value of £320,000.

STANNOUS COMPOUNDS

STANNOUS OXIDE : SnO (Tin Monoxide). This is a black powder which is formed on heating stannous hydroxide in a current of CO_2, and readily oxidises in the air, forming stannic oxide, SnO_2.

STANNOUS HYDROXIDE : $Sn(OH)_2$. This compound is obtained as a white precipitate by the action of sodium carbonate on a solution of stannous chloride.

$$SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2NaCl + CO_2.$$

It is insoluble in NH_3, but dissolves in sodium hydroxide, forming **Sodium Stannite,** Na_2SnO_2, which is transformed on heating into soluble **Sodium Stannate,** Na_2SnO_3, with separation of metallic tin.

STANNOUS CHLORIDE : $SnCl_2$. This compound is obtained on treating tin with the calculated quantity of HCl according to the equation, $Sn + 2HCl = SnCl_2 + H_2$, and crystallises with $2H_2O$, forming common *tin salt*, which loses water at 100°, melts at 250°, and distils unaltered at 606° with a vapour density corresponding with the formula, Sn_2Cl_4, whilst at 900° it corresponds with $SnCl_2$. It is soluble in a little water, more especially in presence of HCl, and is a strong reducing agent (p. 690); with much water a white powder of the oxychloride, SnOH·Cl, is formed, this being also formed together with $SnCl_4$ on allowing a slightly acid solution to stand in the air. Stannous chloride is decomposed by strong H_2SO_4 with evolution of HCl. It also forms double salts such as $SnCl_2$, 2KCl.

It is used as a mordant. Germany produced 810·5 tons in 1905.

The value of the tin produced in the *Transvaal* was £50,000 in 1907, £96,000 in 1908 and £238,000 in 1909.

The consumption of tin in the different countries is as follows (tons):

Country	1908	1909	1910	1911	1912
Germany	—	17,100	18,100	18,300	21,700
France	—	7,300	7,330	7,400	7,500
Austria-Hungary . . .	—	4,100	4,200	4,000	3,800
England	19,600	17,800	21,100	21,900	21,500
Belgium	—	1,320	1,550	1,700	1,300
Russia	—	2,200	2,000	1,900	2,600
Italy	—	2,500	2,600	2,400	2,500
Switzerland	—	1,200	1,200	1,200	1,400
Spain	—	1,030	1,150	1,300	1,200
Sweden, Norway, and Denmark	—	1,300	1,400	1,300	1,400
Netherlands	—	250	250	250	250
Other European countries .	—	900	1,000	1,200	1,000
United States	—	42,800	49,900	48,000	51,700
Other American States . .	—	1,800	2,100	2,300	3,300
Australia	—	900	1,100	900	1,200
Africa	—	500	500	500	600
China	—	2,600	2,680	1,990	2,000
Total World's Consumption.	—	105,600	127,300	117,400	120,600

STANNOUS SULPHIDE : SnS. This is precipitated as a brown, amorphous powder on treating a stannous salt with H_2S, or as a blue crystalline powder on melting tin with sulphur. It is insoluble in alkali sulphides, but dissolves in polysulphides in the hot to form a sulphostannate : $SnS + Na_2S_2 = Na_2SnS_3$. On treatment with HCl, H_2S is evolved and $SnCl_2$ is formed.

STANNIC COMPOUNDS

STANNIC OXIDE (Tin Dioxide) : SnO_2 (Stannic Anhydride). This is found in nature as *cassiterite* of sp. gr. 6·8, and is also formed on heating molten tin in the air. It is a white amorphous substance which melts only at the temperature of the electric furnace. It is insoluble in alkalis and acids. When fused with NaOH it forms soluble stannates.

Italy imported 32·5 tons in 1907, 57·3 tons in 1909, of the value of £8240, 54·1 in 1911, 60·7 in 1913, 59 in 1914, 35·6 in 1916, and 15 in 1917, and exported 102·3 tons in 1916 and 77 tons in 1917.

STANNIC HYDROXIDE. The compound $Sn(OH)_4$ is not known, but the *meta-hydroxide*, H_2SnO_3, has been well studied. It has an acid character and occurs in two modifications :

α-Metastannic Acid forms as a white precipitate on treating a solution of stannic chloride with NH_3 or NaOH, or an alkali stannate with HCl :

$$SnCl_4 + 4NaOH = 4NaCl + H_2O + H_2SnO_3.$$

This compound is soluble in alkalis, and in strong HNO_3 or HCl.

β-Metastannic Acid is formed on treating tin with strong nitric acid. It is insoluble in alkalis and only combines with an excess of these to form sodium metastannate, which is soluble in water, but not in alkali. On heating with HCl it forms **Metastannic Chloride, $SnCl_4$,** which is not identical with the ordinary stannic chloride, and is insoluble in strong HCl, but soluble in water.

The β-acid is transformed into the α-acid on boiling or on fusing it with alkali hydroxides. The β-acid is probably a polymeride of the α-acid. According to W. Mecklenburg (1909) the various varieties of stannic acid are best accounted for by supposing that they consist of particles of varying size, which separate from the alkaline, acid, or neutral colloidal solution, and that the α-acid consists of smaller particles than the β-acid.

Amongst the various salts of α-metastannic acid, the sodium salt, $Na_2SnO_3 + 3H_2O$, which is used in dyeing, deserves mention. It is more soluble in cold than in hot water, and is obtained on fusing the oxide, SnO_2, with NaOH.

STANNIC CHLORIDE : $SnCl_4$. This is a liquid which fumes strongly in the air and is obtained by the action of chlorine on tin or stannous chloride. It has a specific gravity of 2·27 and boils at 114°. In contact with moisture or a little water it is transformed into a crystalline mass, $SnCl_4,5H_2O$, of the consistency of butter (butter of tin). It is prepared industrially by dissolving granulated tin, obtained by pouring molten tin into water, in concentrated hydrochloric acid of 20° Bé. Stannous chloride of 60° Bé. is thus obtained, and this is then neutralised and heated with 40 per cent. of concentrated HCl of 20° Bé. in presence of a little sodium chlorate as an oxidising agent :

$$3SnCl_2 + NaClO_3 + 6HCl = 3H_2O + NaCl + 3SnCl_4.$$

The resulting solution is placed on the market under the incorrect name of "Pink Salt."

R. Steiger (Ger. Pat. 222,838, 1909) mixes oxide of tin with powdered carbon (2 atoms per mol. of the oxide) and makes the mixture into a paste with water and converts it into briquettes, which are heated at 250° to 350° in a current of CO + Cl, anhydrous $SnCl_4$ distilling over.

To recover it from the waste liquors from silk dyeing (in which it is largely used as weighting for the silk), these are first treated with the calculated quantity of sulphuric acid to remove the lime, the filtrate being brought up to 50° Bé. with anhydrous chloride.

It is advantageously prepared to-day by the Goldschmidt process (*see above*, Tin) by treating tinplate scrap (tinned iron) directly with dry chlorine gas from liquid chlorine. If the chlorine and the scrap are dry the iron is not attacked (*see also* U.S. Pat. 877,261 of 1908).

According to U.S. Pat. 874,040 of 1907 the tin can be dissolved from the plate with an anhydrous solution of stannous chloride (*see also* Perino, Ger. Pat. 212,757 of 1907 and Fr. Pat. 401,125 of 1909).

On boiling the aqueous solution, HCl and metastannic acid are formed: $SnCl_4 + 3H_2O = SnO_3H_2 + 4HCl$. It is unaltered, on the other hand, by hot sulphuric acid.

Well-crystallised double salts are known, of which *pink salt,* so called on account of its pale pink colour, $SnCl_4,2NH_4Cl$, was at one time much used in dyeing and in weighting silk. It may be considered as the ammonium salt of *chlorostannic acid,* H_2SnCl_6, and is obtained by saturating an aqueous solution of 2 parts of tin salt, $SnCl_2,2H_2O$, with chlorine, and then pouring the whole into a hot solution of 1 part of NH_4Cl in 2 parts of water. The concentrated aqueous solution does not decompose on heating, but when dilute metastannic acid separates. Solid pink salt costs £80 per ton, and in solutions of 50° Bé. £44 16*s.* Stannic chloride, crystallised or in solution, is usually placed on the market to-day under the denomination of pink salt.[1]

Italy imported 2·9 tons of stannic chloride in 1906, 29·2 tons in 1907, 84·2 tons in 1908, 172·2 in 1909, of the value of £16,532, 165·5 in 1910, 332·9 in 1911, 480 in 1912, 546·5 in 1913, 509·6 (almost entirely from Germany) in 1914, 122·7 in 1915, 369·5 in 1916, and 244·7 (almost entirely from U.S.), worth about £40,000, in 1917.

In 1905 Italy produced 250 tons of pink salt, 200 (£8400) in 1907, and 295 in 1915; in 1916 the Fabbrica Lombarda di Prodotti chimici alone produced 286 tons.

STANNIC SULPHIDE : SnS_2 (Mosaic Gold). This is formed as a yellow amorphous mass by the action of H_2S on solutions of $SnCl_4$, in the form of light scales of a golden colour. It is also obtained on heating 18 parts of tin amalgam (12 parts of molten tin and 6 parts of Hg) with 7 parts of sulphur and 6 parts of NH_4Cl; HgS and NH_4Cl then distil and "mosaic gold" remains, which is used for imitation gilding of many objects—cornices, etc.

It is soluble in strong HCl, forming $SnCl_4$. With HNO_3 it forms metastannic acid. It is soluble in alkali sulphides, with which it forms thiostannates (SnS_3Na_2), from which SnS_2 is reprecipitated by acids. When freshly precipitated it dissolves in aqueous ammonia to form a red liquid which is decolorised by the air and separates **Tin Oxysulphide, SnSO,** with acids. The latter is a white powder, soluble in ammonium carbonate.

[1] Table showing the densities and concentrations of solutions of stannic chloride at 15°

Degrees Bé.	Specific gravity	$SnCl_4 + 5H_2O$ Per cent.	Degrees Bé.	Specific gravity	$SnCl_4 + 5H_2O$ Per cent.	Degrees Bé.	Specific gravity	$SnCl_4 + 5H_2O$ Per cent.
1·7	1·012	2	26·6	1·2268	34	50·5	1·538	66
3·3	1·024	4	28·1	1·242	36	52	1·563	68
4·8	1·036	6	29·6	1·259	38	53·5	1·587	70
6·2	1·048	8	31·2	1·2755	40	54·9	1·614	72
7·9	1·059	10	32·6	1·293	42	56·4	1·641	74
9·6	1·072	12	34·2	1·310	44	57·8	1·669	76
11·1	1·084	14	35·7	1·329	46	59·4	1·698	78
12·5	1·097	16	37·2	1·347	48	60·8	1·727	80
14·2	1·110	18	38·7	1·366	50	62·2	1·759	82
15·8	1·1236	20	40·2	1·386	52	63·8	1·791	84
17·3	1·137	22	41·7	1·406	54	65·2	1·824	86
18·9	1·151	24	43·2	1·426	56	—	1·859	88
20·3	1·165	26	44·6	1·447	58	—	1·893	90
22	1·180	28	46	1·468	60	—	1·932	92
23·5	1·195	30	47·5	1·491	62	—	1·969	94
25	1·210	32	48·9	1·514	64	—	1·988	96

LEAD: Pb, 207.1

This element is found abundantly in nature in *Galena*, PbS, and in smaller quantities in *Cerussite*, $PbCO_3$, in *Crocoite*, $PbCrO_4$, *Wulfenite*, $PbMoO_4$, and *Anglesite*, $PbSO_4$. The greater quantity of lead is obtained from galena, which abounds in the United States, Spain, Germany, and England. Its extraction is not very difficult and is carried out by various methods. The most abundant deposits of lead ores in Italy are in Sardinia (Iglesias), where, after preliminary treatment, the final smelting occurs at Pertusola (Spezia) and at Battino (Serravezza). Much less important galena deposits are found in Venetia, Lombardy, and Tuscany.

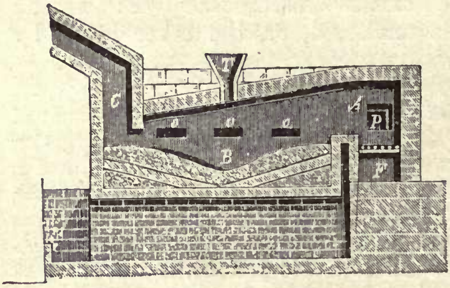


Fig. 312.

(1) EXTRACTION BY ROASTING AND SMELTING. This process is used when the ore is pure and contains no silica, or less than 4 to 5 per cent. The ore is first roasted in a reverberatory furnace and the lead sulphide thus transformed partially into the oxide, PbO, and partially into the sulphate, $PbSO_4$, whilst a portion remains unaltered. On then raising the temperature considerably these three products react with one another, yielding molten lead, whilst SO_2 is evolved:

$$PbS + PbSO_4 = 2Pb + 2SO_2, \text{ and also } PbS + 2PbO = 3Pb + SO_2.$$

The unaltered lead sulphide is again roasted and smelted until completely extracted. The smelting furnace (Fig. 312) is that which has been used for some time in England. The hearth is lined with molten slag and inclined towards the middle, *B*, and also towards one side, so that the molten lead may readily be collected. The mass is kept stirred through the openings, *o*, and is heated by the fuel which burns in *F*. The ore is charged in through the funnel, *T*. The operation lasts 6 to 7 hours for each 800 to 1000 kilos. The crude lead obtained by these various processes still contains considerable quantities of impurities and is known as "work-lead."

(2) PROCESS OF ROASTING WITH REDUCTION. This is the process commonly used, especially in North America, and is suitable for all grades of ore, even when poor and very impure. The ore is first roasted in the usual reverberatory furnaces with the addition of SiO_2 as a flux, until nothing remains but PbO and lead silicate. The mass is then mixed with half its weight of coke and reduced in special cupola furnaces, constructed of sheet iron with double walls (Fig. 313) between which cold water circulates. During the smelting process, compressed air is injected through tubes which pass in at the bottom of the furnace. In order to be able to obtain the metal from an ore which is difficult to reduce, lime or iron ore is added.

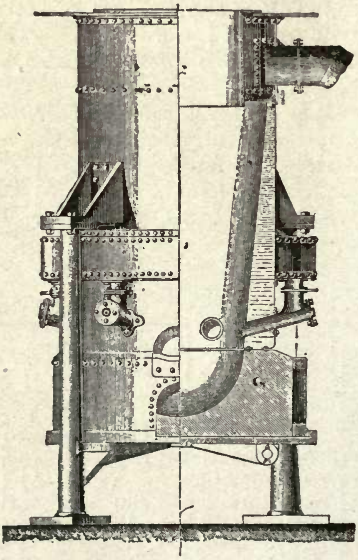


Fig. 313.

An improvement (Huntington and Heberlein) which facilitates the reduction and roasting without loss of lead vapour and without formation of lead sulphate or compact stony masses, consists in roasting the galena at 700° in a mechanical furnace with 6 to 15 per cent. of lime, (CaO), 6 per cent. of fuel, and an excess of air. Fifty to 60 tons of ore are treated in each furnace in 24 hours. $PbSO_4$, $CaSO_4$, a little PbO, but no lead, are formed. The roasting of the product, which contains 1·5 per cent. of sulphur, is completed in a converter (*see* Iron) of 15 tons capacity, into which air is blown for 4 to 6 hours, after which PbO and $CaSO_4$ alone remain, SO_2 being evolved. After this treatment the reduction in the cupola furnace takes place much more easily.

CaO acts as a catalytic agent and does not form calcium plumbate, as was once believed, as iron oxide produces the same effect. Galena may also be roasted directly in a converter with 10 to 35 per cent. of $CaSO_4$ (Carmichael process) by means of compressed air, and is then reduced in the usual manner, but this method is most suitable for ores containing little sulphur.

(3) **PRECIPITATION PROCESS.** This is now little used, but serves well in the case of ores containing much silica. The galena is melted together with a substance which readily removes the sulphur, such as iron (that is, its oxides), $PbS + Fe = Pb + FeS$. The operation is conducted in a cupola furnace such as is used for copper, but the necessary temperature is so high that appreciable loss of lead occurs.

(4) **ELECTROLYTIC PROCESS.** The powdered galena is placed in capsules of hard lead and dilute sulphuric acid is added. The lead sulphide forms the cathode and the bottom of the capsule the anode. When the current is passed, H and H_2S are evolved and the lead collects as a spongy mass (*see later*).

REFINING OF WORK-LEAD. The crude lead obtained by the various processes contains considerable quantities of impurities, and is purified by liquation (p. 517) if the lead contains copper (*see* Treatment of Copper), or by oxidation, the crust or scum which forms on the surface of the molten lead being separated; or the lead may be reduced by means of poles of green wood (*see* Copper, p. 696).

Numerous electrolytic refining processes have also been proposed, lead fluosilicate being very suitable for electrolysis, as it yields compact blocks of lead at the cathode. The formation of crystals is avoided by adding a little gelatine to the bath.

In the Trail works (British Columbia) about 75 tons of electrolytically refined lead were produced daily in 1910, 240 asphalt-lined wooden vessels (0·9 × 2·4 × 1·05 metres) being arranged step-wise in six double batteries. Each vessel contains 20 168-kilo cathodes suspended from current-leads of copper bar; alternating with the cathodes are 21 anodes in the form of thin strips (15 mm.) of pure lead. The electrolytic bath is prepared from fluorspar, quartz, and sulphuric acid in a cast-iron vessel, the gases evolved being condensed in a tower by means of water, which is circulated until it contains 30 per cent. of hydrofluosilicic acid.

The electrolyte is formed of lead fluosilicate and free hydrofluosilicic acid, and contains 12 per cent. SiF_4 and 5 to 6 per cent. Pb. The current density is 16 amps. per 0·0929 sq. m. of cathode surface, and the voltage 0·32, which is reduced to 0·02 volt with the contacts. The addition of 180 vessels, to reduce the current density to 12 amps., is projected. The anode residues, which constitute 15 per cent. by weight, contain 35 per cent. Ag, 25 per cent. Sb, 20 per cent. As, and 8 per cent. Cu, and are remelted. The lead obtained has a purity of 99·993 per cent. (mean of 2000 tons).

PROPERTIES. Pure lead (refined lead of 99·99 per cent. Pb) has a bluish-grey colour, is very soft and ductile, and in the air becomes covered with a thin layer of oxide which destroys this lustre but protects it from atmospheric corrosion. It has a specific gravity of 11·37, melts at 327°, and boils at 1600°. When lead is obtained in a state of extremely fine division, for instance, by igniting lead tartrate or citrate in a test-tube out of contact with the air, it catches fire spontaneously and is then known as *pyrophoric lead* (p. 189). It is not attacked by HCl or H_2SO_4 in the cold, because the first layer of insoluble lead chloride or sulphate formed at the surface protects the rest of the metal, but if the lead is very finely divided it is completely attacked. Even acetic acid and other organic acids attack lead, and nitric acid dissolves it in the cold, forming the nitrate; it is attacked more easily by nitric acid rich in nitrous vapours than by the pure acid. Zinc and iron separate crystalline lead from solutions of its salts. If a zinc rod is placed in a vessel containing a solution of lead acetate, the zinc quickly becomes covered with many lustrous and branching crystals of lead (lead tree).

Lead salts are poisonous, and lead should therefore be absent from all utensils used for the preparation of food, so that solders containing lead and earthenware glazed with lead should be avoided (*see* Lead Poisoning, in the section on White Lead); it should also be avoided for water-pipes (p. 233).

USES AND STATISTICS. Large quantities of lead are used in various chemical industries, but especially for sulphuric acid tanks, lead chambers, the manufacture of hard lead (pp. 284 and 428), pipes, small shot (containing 0·2 to 0·8 per cent. of arsenic), and certain important alloys, such as solder and type metal (p. 428), etc. The electrical accumulator and cable industries and the lead piping and sheet industries consume about one-fourth of the total lead; the white lead industry uses about 30,000 tons of lead per annum.

The *world's production* of lead was 380,000 tons in 1880, and 586,000 tons in 1890; other statistics are shown in the Table.[1]

---

[1] Production and consumption of crude **Lead** in different countries (in thousands of tons):

Country		1900	1905	1909	1910	1911	1912	1913	1914	1915	1916
United States	prod.	253	291	335	355	364	374	395	—	—	—
	con.	—	—	—	373	358	—	—	—	—	—
Germany	prod.	122	153	168	160	161	165	181	—	—	—
	con.	—	—	—	210	230	—	223	—	—	—
Spain	prod.	173	181	184	192	172	196	—	—	—	—
	con.	—	—	—	9	10	—	—	—	—	—
Mexico	prod.	64	75	118	121	124	110	—	—	—	—
Australia	prod.	87	107	77	99	100	107	—	—	—	—
	con.	—	—	—	7	9	—	—	—	—	—
Asiatic Turkey	prod.	—	—	—	13	12	13	—	—	—	—
France	prod.	15·2	24	27	20	23	31	28	—	—	—
	con.	—	—	—	90	99	—	108	—	—	—
Sweden	con.	1·4	0·6	0·2	0·4	1·2	1	1·2	—	—	—
Belgium	prod.	16	23	41	40	44	55	36	—	—	—
	con.	—	—	—	32	40	—	42	—	—	—
Austria-Hungary	prod.	12	15	14	17·4	19·4	22	23	—	—	—
	con.	—	—	—	32	36	—	36	—	—	—
Great Britain	prod.	35	28	31	30	27	26	30·5	—	—	—
	con.	—	—	—	208	199	—	191·4	—	—	—
Greece	prod.	17	14	15	17	14	15	—	—	—	—
Canada	prod.	29	26	23	15	11	16	17	—	—	—
	con.	—	—	—	12	21	—	—	—	—	—
Japan	prod.	2	2·3	3·4	3·9	4	3·6	—	—	—	—
	con.	—	—	—	19	19	—	—	—	—	—
Italy	prod.	24	19	22	15	17	20	22	21	22	24
	con.	—	—	—	28	36	—	—	—	—	—
Russia	prod.	0·2	0·7	0·8	1·3	1	1	1	—	—	—
	con.	—	—	—	49	43	—	59	—	—	—
Other Countries		37	41	30	40	—	—	—	—	—	—
World's Production		849	989	1056	1093	1069	1189	1187	—	—	—

The crude lead imported into Germany in 1910 amounted to 75,000 tons.

England, in 1910, produced 28,500 tons of concentrated lead ores, 24,282 in 1913, and 26,013 in 1914, and imported 233,410 tons of crude lead and lead ore together, 21,500 tons of the lead being from the ore of British colonies; in the same year 67,000 tons of lead were exported, so that the British consumption was 187,000 tons. In 1913 186,000 tons were exported, in 1914 204,000, and in 1915 226,000. The output of lead ore was 29,744 tons in 1909 and 28,534 tons (£232,000) in 1910.

United States. About one-fifth of the lead produced in 1912 was obtained from imported ore; in the same year 12,000 tons of lead-antimony alloys were produced. In 1909 110,000 tons of lead were imported, and in 1912 only 81,000 tons (especially as ore from Mexico). In 1913 the production of lead-antimony alloys was 15,000 tons.

The *Argentine* in 1909 imported lead to the value of £112,000.

France in 1913 exported 14,263 tons of lead and imported 39,772 tons of lead ore, in 1914 8200 and 21,780, and in 1915 48 and 15,990 tons represented exports and imports respectively.

The figures for the lead and lead ore industry (including alloys with Sb, scrap, sheet, and piping) in Italy are as follows (tons):

		1905	1908	1910	1911	1912	1913	1914	1915	1916	1917
Importation		6,764	11,741	14,500	20,200	15,627	11,494	9,827	17,326	14,358	26,288
Exportation		—	—	933	627	4,121	577	1,271	145	156	110
Lead ore	prod.	—	—	36,540	33,958	41,680	44,654	43,538	41,590	39,460	—
	imp.	—	5,620	1,426	6,042	12,391	9,552	5,736	6,181	12,551	4,838
	exp.	—	2,041	4,122	15,791	17,062	16,950	15,402	3,817	9,871	7,622

Spain produced the following quantities of lead ore: 285,266 tons in 1915 and 260,282 £12,865) in 1916; the exports of argentiferous lead were 2935 tons in 1915 and 7371 (£14,403) in 1916, and the imports 172,472 tons in 1915 and 147,407 tons (£5,370,167) in 1916.

The price was £16 16*s.* per ton in 1880, and about £12 8*s.* in 1902; it then oscillated between a minimum of £12 in 1904 and a maximum of £20 in 1906; in 1908 it varied from £14 12*s.* at the end of January to £12 12*s.* in July, and to £13 12*s.* in December; in 1909 it fluctuated from £13 4*s.* to £12 10*s.*, and then to £13, and in 1910 from £13 18*s.* and then to £13. In 1917, during the European War, the price in Italy rose to £120 per ton.

Until 1910 there existed an international syndicate of European, American, and Australian producers, but it did not work very regularly.

Italy imported 6764 tons of lead (including alloys with Sb) in 1905, 10958 in 1906, 11,741 in 1908, and 10,011 (£144,000), to which must be added 250 tons (£11,200) of sheet, piping, printing type, etc., in 1909; *see also* Table in footnote.

The output of lead ore in Italy was 46,650 tons (£267,268) in 1908 (*see* Note).

LEAD COMPOUNDS

In its more stable derivatives lead is divalent, but less stable tetravalent compounds exist, and it forms five oxides.

A more sensitive reaction for detecting traces of lead than that with sulphuric acid or hydrogen sulphide (blackening) is the one suggested by W. N. Iwanow (1914) for its detection in ordinary water; 50 c.c. of water is treated with 50 c.c. of a fresh 2 per cent. solution of sodium bisulphite; if a milky turbidity forms after some minutes, lead is present to the extent of one per million of the water. The test is not invalidated by the presence of Cu, Ag, Ni, Fe, Al, Mg, and Ca, but Sn and Ba should be absent.

LEAD SUBOXIDE : Pb_2O, is a black powder which is converted on heating into the more stable oxide, PbO.

LEAD MONOXIDE : PbO. On heating lead for a prolonged period in the air (or on heating the hydroxide, nitrate, or carbonate) an amorphous yellow powder of PbO is formed, the common name for which is **Massicot.** On melting massicot and then allowing it to cool more or less rapidly a more or less reddish-yellow scaly mass of PbO results, which is called **Litharge.** This is obtained in large quantity in the extraction of silver (p. 707), and in the preparation of sodium nitrite (p. 579); in the latter case it is obtained pure, whereas that given by oxidation of lead always contains 8 to 10 per cent. of the metal. According to Fr. Pat. 409,944 of 1909, pure PbO is obtained by heating at 300° to 400° lead pulverised in a current of air and steam. Lead oxide has a markedly basic character and saponifies the fats. It is slightly soluble in water, with which it forms the hydroxide; it dissolves in caustic potash solution, from which it crystallises in rhombic prisms. It has a specific gravity of 9·2 to 9·5 and is easily reduced to lead by H, CO, or carbon on heating. PbO is used for the preparation of many other lead compounds, such as the acetate, etc., for glazes, in glass-making, and in the manufacture of earthenware. Crude litharge costs about £16 per ton; when refined it costs double. Massicot costs £26 to £28. In general the prices vary with those of lead.

France exported 523 tons and imported 322 tons of lead oxide in 1913, the amounts for 1914 being 387 and 314 tons, and for 1915, 459 and 134 tons respectively.

The *Italian* trade is as follows (tons):

	1903	1905	1908	1910	1911	1912	1913	1914	1915
Production .	883	580	780	730	735	517	578	553	721
Importation .	—	600	883	736	*See* also *minium*, p. 787.				
Exportation .	—	—	100	62					

In 1905 Germany exported 4450 tons of litharge at £15 per ton.

LEAD HYDROXIDE : $Pb(OH)_2$. On adding sodium hydroxide or NH_3 to a solution of a lead salt a voluminous white precipitate of lead hydroxide is produced which is soluble in an excess of sodium hydroxide, but insoluble in excess of ammonia. It is slightly soluble in water, has an alkaline reaction and absorbs CO_2 from the air, forming a basic lead carbonate, that is, a mixture of hydroxide and carbonate which is used in painting under the name of *white lead.* At 130° it decomposes into H_2O and PbO.

MINIUM : Pb_3O_4 (Red Lead or Red Lead Oxide). This is one of the oldest artificial colouring matters, and was prepared in the time of Pliny by heating white lead in the air and even then was used to adulterate cinnabar. It is obtained by heating PbO or residues from the manufacture of sodium nitrite (p. 579) carefully in a reverberatory or muffle furnace at about 450° in such a manner that they do not melt, but the best qualities of minium are obtained by heating the pure oxide with sodium nitrate or potassium chlorate in an oxidising flame to a dark red heat, or by heating lead sulphate mixed with the nitrate and sodium carbonate.[1] It has a bright scarlet colour and may be considered to have the constitution, $2PbO + PbO_2$; in fact on treatment with HNO_3, PbO is dissolved and PbO_2 remains. It has a specific gravity of 8·6 to 9.

On heating strongly it first becomes dark red, then violet, and finally almost black, and on cooling regains its original colour.

According to J. Milbauer (1909) the reaction $3PbO + O \rightleftarrows Pb_3O_4$ tends, as the temperature rises, towards an equilibrium with formation of a maximum of 37 per cent. of Pb_3O_4 at about 500°, only one-half this amount being formed at 375° or even at 390°. The duration of the heating influences the amount formed, twice as much being obtained in six hours at 480° as in three hours; further heating increases the yield but little. The presence or absence of moisture and the rate of flow of the oxygen are without effect, but the partial pressure or concentration of the oxygen exerts considerable influence. Oxygen at 100 per cent. gives double as much Pb_3O_4 as that at 80 per cent., three times as much as that at 60 per cent., six times as much as that at 40 per cent., and 65 times as much as that at 20 per cent. Stirring of the mass during heating and also preheating of the air or oxygen have little effect. Mixing of the PbO with inert substances (*e. g.*, SiO_2) lowers the yield, but ordinary impurities are of slight influence.

The reaction between lead carbonate and oxygen at 470° is almost complete after three hours (89·9 per cent. Pb_3O_4; 80 per cent. after two hours), and undergoes no further change in seven hours (89 to 90 per cent.); the temperature affects the yield greatly, 30 per cent. of Pb_3O_4 being formed at 370°, about 90 per cent. at 470°, and only 68 per cent. at 535°.

The dissociation of Pb_3O_4 into $3PbO + O$ begins at 500° and is complete at 580° in three hours; in a vacuum, however, the whole is decomposed in seventy-five minutes at 550°.

In practice the best yield (89 per cent.) of minium is obtained by heating first at 500°, since the reaction is then very rapid (3 to 4 hours instead of 25 to 30 hours), and finally for 3 to 4 hours at 460°. With compressed air at 8 to 12 atmos. the process is still more rapid.

Powdered minium is used with oil in painting and for coating machinery, piping, and beams of iron to prevent rusting. It is also used in glass manufacture, etc. It is now partially replaced by red iron oxide, Fe_2O_3. It costs from £14 to £20 per ton according to its purity and the price of lead. The impurities are represented by the residue insoluble in dilute nitric acid mixed with aqueous sugar solution. Sometimes it is coloured artificially with a coal-tar colour, which is dissolved out by alcohol. The best minium contains

---

[1] This method yields always a mixture of Pb_3O_4 with PbO (*see later*), and to obtain pure Pb_3O_4 the PbO may be dissolved out with 10 per cent. lead acetate solution; hot 10 per cent. lead nitrate solution may also be used as solvent for the oxide and carbonate, but the purity of the Pb_3O_4 is then not so high; best of all is boiling 50 per cent. KOH solution. To obtain Pb_3O_4 of 100 per cent purity, potassium nitrate is heated to 340°, a little less than the theoretical quantity of PbO_2 being added in small quantities; the temperature is kept at 340° until evolution of oxygen ceases, when it is raised to 480° (not more), and the fused mass poured into a porcelain plate and, when cool, powdered and washed with hot water until the reaction for nitrates ceases; the pure residue is dried at 110°.

Bellucci and Parravano (1906) obtained pure Pb_3O_4 by saturating hot caustic potash solution with lead peroxide in a silver or platinum dish and allowing the mass to cool for some days in a desiccator. The crystals of potassium orthoplumbate which separate (the mother-liquors serve to dissolve more PbO_2) are spread on porous porcelain and are afterwards dissolved in concentrated caustic potash, addition of PbO_2 to the boiling solution then causing (when $2PbO_2$ is added per 3PbO) a red precipitate of pure Pb_3O_4.

Brauner (1887) and Milbauer (1914) obtained pure Pb_3O_4 by treating dilute lead nitrate solution with dilute hydrogen peroxide and dissolving in the hot the hydrated lead peroxide which separates; Pb_3O_4 slowly separates out. In any case, to obtain pure minium by the wet way, caustic potash solution containing at least 150 grams of KOH in 100 c.c. is used, and the oxides of lead dissolved are exactly in the proportion, $3PbO + 2PbO_2$.

only 1 per cent. of impurity, and the ordinary quality up to 10 per cent., while products with not more than 50 to 70 per cent. of true minium are often sold.

The trade in *Italy* is as follows (tons):—

	1906	1908	1910	1911	1912	1913	1914	1915	1916	1917
Production .	1400	1600	—	1840	1684	1765	1630	2066	—	—
Importation .	828	834	736	724	546	524	465	164	19	12
Exportation .	101	106	62	84	34	103	58	30	90	124

The figures for the importation and exportation in 1911 and subsequent years include also litharge.

Germany exported 8900 tons of minium at £1 16*s.* per ton in 1905, and 9114 in 1909, when the imports were 1193 tons.

LEAD DIOXIDE, BROWN LEAD OXIDE : PbO_2. This compound is also inappropriately called *lead peroxide.* It is obtained on treating red lead with dilute HNO_3:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O,$$

or by passing chlorine into an alkaline solution of a lead salt, or by adding calcium hypochlorite to a solution of a lead salt:

$$2PbCl_2 + Ca(OCl)_2 + 2H_2O = CaCl_2 + 2PbO_2 + 4HCl,$$

the hydrochloric acid formed combining with the lime. It is now also prepared electrolytically from lead nitrate. PbO_2 is an amorphous powder of dark brown colour.

With cold HCl it forms lead tetrachloride, $PbCl_4$. PbO_2 readily evolves oxygen on heating, being transformed into PbO, and with hot KOH it forms **Potassium Plumbate, K_2PbO_3,** which thus shows an analogy with potassium stannate. Potassium plumbate is decomposed by much water into KOH and PbO_2. A **Calcium Plumbate, $CaPbO_3$** or **Ca_2PbO_4,** is obtained on heating a mixture of PbO and $CaCO_3$ in the air to 700°, CO_2 being evolved. On heating the plumbate to 700° in presence of pure CO_2 oxygen is evolved and calcium carbonate and PbO are formed, which then regenerate the plumbate in contact with air. A continuous process for manufacturing oxygen can be based on this process and was applied industrially by Kassner in 1900 (*see* p. 198).

Lead dioxide is of great importance in connection with the manufacture of electric accumulators (p. 525), as an energetic oxidising agent in various chemical processes, and also in the manufacture of matches. The commercial product of 80 per cent. strength costs £38 per ton, whilst the more concentrated product of 96 to 98 per cent. costs £46, and when purified £128 to £160.

In 1905 Italy produced 1 ton, in 1908 20 tons, of the value of £480, in 1911 58 tons, in 1914 27 tons, and in 1915 26 tons.

LEAD CHLORIDE : $PbCl_2$. This is formed as a white precipitate by the addition of dilute HCl or NaCl to a fairly strong solution of a lead salt. It is very slightly soluble in cold water, but dissolves in 30 parts of water at 100°, and separates in white, shining crystals on cooling this solution. The separation of $PbCl_2$ is facilitated by the addition of dilute HCl, which increases the concentration of the Cl' ions until the concentration product exceeds the solubility of $PbCl_2$ (pp. 103 and 706).

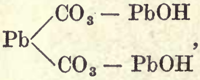
LEAD TETRACHLORIDE : $PbCl_4$. On dissolving $PbCl_2$ in concentrated HCl and saturating the solution with chlorine, a heavy yellow oil of sp. gr. 3·18 separates, this consisting of $PbCl_4$. On heating this product $PbCl_2$ and Cl_2 are formed, and with NH_4Cl it forms a yellowish, crystalline double salt, $PbCl_4,2NH_4Cl$, which is analogous to pink salt (p. 780).

LEAD IODIDE : PbI_2. This compound is obtained from a solution of a lead salt by the addition of potassium iodide and forms yellow crystals soluble in hot water to a colourless solution.

LEAD NITRATE : $Pb(NO_3)_2$. This compound is obtained in a crystalline condition by concentrating a solution of lead or PbO in dilute nitric acid. It is isomorphous with barium nitrate. 100 parts of water at 10° dissolve 48 parts, and at 100° 140 parts of the nitrate. On heating the solid salt it decomposes into $PbO + 2NO_2 + O$. It is used, mixed with PbO_2, for match-heads and fireworks, and also to some extent in the printing of textile fabrics, etc. It costs £40 to £48 per ton. Fifty-three tons were produced in Italy in 1905, 86 tons, of the value of £2864, in 1907, and 10·5 tons in 1915.

LEAD SULPHATE : $PbSO_4$. This compound is found in rhombic crystals as *anglesite*, and is isomorphous with barium sulphate. It is formed as a white, heavy, insoluble crystalline mass on adding sulphuric acid or a soluble sulphate to a soluble lead salt. It is slightly soluble in strong H_2SO_4 (p. 284), and in concentrated alkalis, basic lead sulphate being formed, $2PbSO_4,Pb(OH)_2$ (*see* White Lead). It dissolves in ammonium tartrate and sodium thiosulphate solutions. It is soluble in water only to the extent of 1 part in 12,135 parts both on heating and in the cold. When heated with sodium carbonate it forms $PbCO_3$, and it is reduced by carbon at a red heat to PbS.

LEAD PERSULPHATE : $Pb(SO_4)_2$. This compound is formed in an impure condition, and mixed with $PbSO_4$, by electrolysing strong H_2SO_4 between two lead electrodes in the cold. It is soluble in concentrated H_2SO_4 and precipitates PbO_2 with water; it is thus an energetic oxidising agent.

LEAD CARBONATE : $PbCO_3$. This is obtained as a white, insoluble, heavy mass on treating lead nitrate with ammonium carbonate or lead acetate with CO_2. It is found naturally as *cerussite.* **Basic Lead Carbonate**, which forms *common white lead*,  $Pb\begin{cases} CO_3 - PbOH \\ CO_3 - PbOH \end{cases}$, is much more important, having been used in paint (for artistic and other purposes) since ancient times, as it has very good covering power, that is, compared with other white mineral pigments it covers a larger surface of wood when suspended in linseed oil, forming a perfectly white surface through which the wood which it covers can no longer be seen. There are various forms of apparatus for comparing the covering powers of different pigments. White lead has, however, the disadvantage that it is poisonous and that it is blackened by hydrogen sulphide vapours, as it then forms black PbS. For these reasons it is gradually being replaced by zinc oxide and antimony oxide.[1]

PROPERTIES OF WHITE LEAD. It is a heavy white powder, insoluble in water, but completely soluble in dilute nitric acid, in which such impurities as barium, lead and calcium sulphates and silica are insoluble; the presence of calcium may be detected by treating the nitric acid solution with ammonia, filtering and precipitating the lime with ammonium oxalate, and the presence of zinc sulphide by the evolution of H_2S when the pigment is treated with HCl. Commercial white lead contains 84 to 87 per cent. of combined PbO (theoretically, 86·32 per cent.), and 11 to 15 per cent. of combined CO_2 (theoretically 11·35 per cent.), but qualities with as much as 14 per cent. are inferior.

Mixtures of white lead with barium sulphate and other substances are sold under various names (Genoa white, Venetian white, Hamburg white, Dutch white, English white, etc.). To detect even 0·1 per cent. of free lead oxide in white lead, a small quantity of the latter is mixed on a watch-glass with a few drops of water and the paste treated with a couple of drops of phenolphthalein solution, which gives a red coloration.

---

[1] The powerful poisonous action of white lead and also of other lead compounds, such as the oxides, acetate, etc., has caused many cases of lead poisoning of workmen employed in industries in which such compounds are used, and laws protecting the workmen from such dangers have therefore been passed in various countries. The symptoms of lead poisoning are anæmia, bright olive-yellow coloration of the skin and of the mucous membranes, wasting of the tissues, dark blue discoloration of the gums, fœtid breath, etc., followed by more serious disturbances, such as lead colic (especially in the case of those who drink alcoholic liquors), cerebro-spinal lead poisoning, and finally delirium, convulsions, coma, paralysis, etc. In England in 1910 there were 669 cases of lead poisoning in works and 263 cases, with 48 deaths among painters. In France the manufacture and use of white lead were prohibited in December 1906, and its prohibition was reinforced by a new law in 1910. In Germany certain regulations for the arrangement and site of the workshops, form of the pans in which the lead is melted, elimination of dust everywhere, the rejection of delicate workmen or those addicted to alcoholism and tobacco, are legislatively prescribed in *Reichgesetzblatt*, May 26, 1903, p. 225, and June 27, 1905, p. 555, in which it is also prescribed that all the workpeople shall bathe every day, change their clothes, not partake of eatables in the workshops, etc. In Italy little or nothing has been done. In 1910 a large hospital for the treatment of industrial diseases was opened in Milan, and in this establishment lead poisoning has been studied and cured by special methods. Frequent washing with dilute alkali sulphide solutions (also sodium sulphide soap) is recommended, these forming lead sulphide which is insoluble and non-poisonous even if ingested (Rambousek and Oliver). In Vienna in 1902 there were 125 well-marked and undoubted cases of lead poisoning amongst painters. It is universally admitted that white lead may always be replaced without inconvenience by other pigments, *e. g.*, by chalk in certain cases, and by zinc oxide and lithopone in nearly all cases; for the protection of iron from rust, use may be made of ferric oxide or colcothar, while for tightening joints in pipes, etc., various asbestos mastics may be employed.

White lead is prepared industrially by various processes which all start from very pure lead and dilute reagents in order to obtain an amorphous (non-crystalline) final product of good covering power. In the *Dutch process,* which is still sometimes used, plates of lead rolled into spirals are placed in receptacles containing a little acetic acid, and these vessels are then placed on shelves surrounded by horse-dung. Through the heat and the carbon dioxide formed by the fermentation of the dung basic lead acetate is first formed, which is then converted into basic carbonate, and in five or six weeks the lead sheet has been converted into white lead which is freed from unaltered lead, lead acetate and other impurities by washing with water. It is then dried in porous vessels or in cakes in the air.

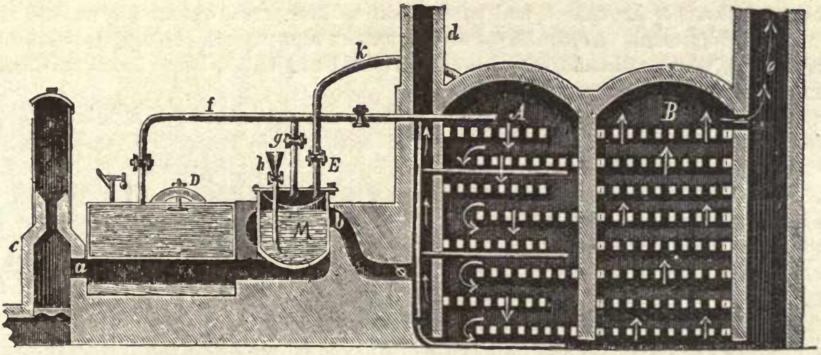


Fig. 314.

In the *German* or *chamber* process lead plates are placed on horizontal gratings in closed chambers, *A* and *B* (Fig. 314), which are constructed of wood or brickwork. Steam and acetic acid vapour first enter these chambers from a boiler, *D*, heated by the hot gases of a coke furnace, *C*. The steam passes through the tubes *f* and *g* and into the pan, *M*, containing acetic acid, which is also heated by the gas from the coke furnace. It thus carries acetic acid vapours with it into the tube *k*, whence it enters the top of the chamber, *A*, in which the temperature is maintained at 50° to 60° for 10 to 20 hours. The basic acetate thus formed on the plates is transformed into basic carbonate by gases containing much CO_2, which pass in from the coke furnace. The operation lasts several days, and the white lead is then removed from the unaltered lead with necessary precautions in closed rooms provided with fans. The crude white lead is worked up to a paste with water in order to separate lead acetate and unaltered lead, and is powdered whilst still moist, or sometimes when dry, in an ordinary flour mill, then passed through sieves and dried in the air or in drying chambers at a gentle heat.

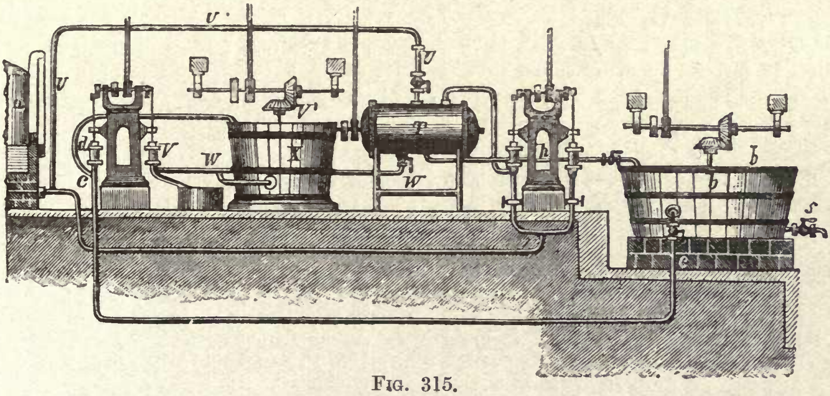


Fig. 315.

According to the *French process,* which was first applied by Thénard in a large works at Clichy, litharge is dissolved in acetic acid in the vat, *X* (Fig. 315), provided with a stirrer, *V′*; by means of the pump *V*, the basic lead acetate formed is passed through the tube *W* into the vessel, *T*, which is provided with a stirrer. Carbon dioxide passes into this from the gasometer, *a*, through the tube *U* until the basic lead acetate is transformed into basic carbonate and neutral lead acetate. The whole mass is then discharged into the large vat, *b*, where the white lead is allowed to settle from the solution of the neutral lead acetate, which is recovered and withdrawn by the pump *c d*, and returned into the vat, *X*, where it is reconverted into the basic acetate by means of fresh lead oxide without further consumption of acetic acid. The white lead deposited in *b* is stirred up with water, discharged through the tube *S* and passed into a filter-press, where it is washed and is then dried and ground. A chamber of 400 cu. metres capacity may be charged with 40,000 kilos of lead, which yields 32,000 kilos of white lead and 13,000 kilos of lead residues, the transformation occupying seven days.

A rapid process using a similar arrangement is that proposed by Wultze in 1904 (Ger. Pats. 173,105, 174,024, 181,399), in which granulated lead is treated with acetic acid and lead acetate in a current of air and then with CO_2 under pressure from a coke-fed producer. The dissolution of the lead is rapid, and in a few hours white lead is precipitated with complete regeneration of the lead acetate, which is used in turn to dissolve new lead without further consumption of acetic acid. This rapid and economical process is used by a works in Austria and another in Germany, in the latter, however, without much success, owing mainly to the large consumption of acetic acid.

By the Wultze process 4000 kilos of lead are transformed completely into 3000 kilos of white lead in a fortnight, and to produce 5000 kilos of white lead per day a vat 7 metres high and with a base of 3 sq. metres is used for the dissolution, and another 5 metres high and with a base of 3 sq. metres for the reaction (*see also* Ger. Pat. 263,471, 1912, F. H. Sharpe).

The process of L. Falk (1909) appears to be more rational and economical, and has already been applied in a Russian works (as an improved and shortened form of the Jarosslaw process (*see later*) and of the older Benson and Gossage process). By this process 100 kilos of neutral lead carbonate (weighed while moist), for example (obtained from basic lead acetate by the action of CO_2 until the reaction is weakly acid), are worked to a paste with 19 parts of water, 1 per cent. of lead acetate (which acts as a catalyst), and 40·5 kilos of lead oxide (prepared at not too high a temperature and added a little at a time). The whole is stirred in the cold with occasional addition of water until the paste gradually hardens. After three to four hours the operation is finished and the famous *Russian white lead* is obtained, which corresponds with the formula, $5PbCO_3,2Pb(OH)_2,PbO$, containing 87·45 per cent. of PbO, 10·78 per cent. of CO_2, and 1·76 per cent. of H_2O; this cannot be formed by the chamber process, since at the temperature there prevailing (60° to 70°) a carbonate so basic is hydrolytically dissociated, so that only a white lead, $2PbCO_3, Pb(OH)_2$, of less covering power, can be obtained.

According to Bronner's process, freshly precipitated lead sulphate is heated to 70° with NaOH and basic lead sulphate thus formed:

$$3PbSO_4 + 2NaOH = 2PbSO_4,Pb(OH)_2 + Na_2SO_4;$$

on then heating with a solution of sodium carbonate, white lead is precipitated:

$$2PbSO_4,Pb(OH)_2 + 2Na_2CO_3 = 2PbCO_3,Pb(OH)_2 + 2Na_2SO_4.$$

Since 1906 use has been made in some of the American works of the Mild process without acetic acid (an improvement on H. Rowley's U.S. Pat. 785,023, 1905): the lead melted in a vessel issues from the base in heated tubes called atomisers, in which it is met by a current of steam, and is thus subdivided into minute particles solidifying on falling into water. This lead paste is pumped to tanks commanding the oxidisers, the water returning to the lower vessel. A certain quantity of the "lead sand" and a certain quantity of water fall into the oxidiser, air being then passed through the mass; in twenty-four to thirty-six hours about 80 per cent. of the lead is converted into various basic lead oxides, which are detached from the unaltered lead by suitable mixers and pumped to the carbonating vats where CO_2 (furnished by coke furnaces and washed to remove ash and sulphur compounds) is passed into the mass. In thirty-six hours basic lead carbonate (white lead) is formed almost exclusively; this is passed as a paste into trays to dry, and, when slightly compressed, then forms a very fine, amorphous powder.

For some years attempts have been made to produce white lead by an *electrolytic* *process* from a feebly alkaline (1½ per cent.) solution of a mixture of sodium chlorate (80 parts), and Na_2CO_3 (20 parts). Soft lead is used as an anode and hard lead as a cathode. The potential difference is 2 volts, and the current density 0·5 amp. per square metre surface of the electrodes.

STATISTICS AND PRICES. The output, etc., of white lead in Italy, is as follows (tons):

	1905	1908	1910	1912	1913	1914	1915	1916	1917
Production .	5010	4645	3778	3074	3639	4409	2706	—	—
Importation .	79	590	489	368	157	67	19	37	25
Exportation .	247	113	135	40	211	629	309	1492	388

Germany exported 16,478 tons of white lead at £16 per ton in 1905, 13,733 in 1908, and 10,607 in 1909; in 1908 the production was 33,000 tons (£760,000), 25,000 being consumed, 11,000 exported, and 3000 imported. In 1909 the output was 38,000 tons.

In Germany the output is almost all from the German chamber system, the Dutch system having nearly disappeared, whereas in England the latter predominates. *Russia* consumed 30,000 tons of white lead in 1909. In the *United States* all the white lead is produced by two large companies, each with a capital of £6,000,000, and in 1903 the output was 113,000 tons, of the value £2,600,000. In 1910 *England* produced 58,000 tons of white lead and imported 145,000 tons, 50,000 tons being used as paint. The British white lead industry employs 2500 persons, the capital invested being £3,000,000; on acetic acid alone £20,000 are spent annually. It is maintained in England that zinc white is unusable for outside paint-work exposed to atmospheric agents, etc. England imported 16,500 tons in 1911 and exported 20,000 tons.

The consumption of white lead in *Russia* in 1910 was estimated at 32,000 tons, and about 12,000 tons are produced in the city of Jarosslaw and its neighbourhood by the old Kubotschny-Spossob process, which consists in mixing sieved litharge (still containing 25 to 40 per cent. Pb) with 4 to 5 per cent. of powdered lead acetate, moistening with water, forming a compressed heap, and leaving overnight. In the morning it is cut with a knife into thin slices and spread on cloths for three days at 40° in a chamber in which CO_2 is slowly evolved from a coke furnace. The mass is again collected, moistened with water, left heaped up overnight, again placed on cloths, and so on, this procedure being continued for three to five months. During the last fifteen days the mass becomes white, highly adhesive and difficult to cut; each heap is made from 250 kilos of litharge. The Jarosslaw white lead thus prepared is renowned for its good quality (it contains less than 11 per cent. CO_2). It is expensive to make, as the process is slow and requires much labour, but it is sold at a higher price than any other quality.

France consumed about 25,000 tons of white lead (and only 6000 of zinc white) per annum at about the end of the last century.

The *world's output* of white lead in 1909 was 255,000 tons, worth £6,200,000.

The *price of white lead* varies according to its purity, because it often contains considerable quantities of barium sulphate. The price of the pure product varies with the price of lead, and thus in Germany it was sold at £18 16*s.* per ton in 1900, £18 in 1905, and £22 in 1907. In Italy, where white lead enjoys a protective tariff of £3 4*s.* per ton, the following prices held on truck at Genoa: £23 4*s.* in 1900, £16 16*s.* in 1902, £15 8*s.* in 1904, £24 in 1906, £27 4*s.* in 1907, £22 in 1908, £18 16*s.* in 1909, and £18 8*s.* in 1910.

LEAD SULPHIDE: PbS. This is found naturally as *galena* (*see above*), and may also be obtained in the form of a black precipitate by passing H_2S into a solution of a lead salt. Even minimal traces of lead may be detected by this extremely delicate reaction, as they produce a brown coloration. The sulphide is oxidised to $PbSO_4$ by HNO_3 and by H_2O_2.

LEAD ARSENATE: $Pb_3(AsO_4)_2$, used largely as an insecticide, may be obtained in the wet way from lead nitrate and sodium arsenate, but more economically in the dry way, by mixing arsenic ores or residues with lead oxide (4·4 PbO per 1AS) and heating in a reverberatory furnace for eight to ten hours and then extracting the comminuted mass with a 25 to 30 per cent. caustic soda solution (1·5 kilo NaOH per 1 kilo of lead arsenate). The liquid is then filtered and the lead arsenate separated from the filtrate by neutralisation with nitric acid, the precipitate being washed, pressed and sold wet (to be pulped and suspended in water before use) or as a dry powder. For emulsification with water the best results are given by *acid lead arsenate,* $PbHAsO_4$, obtained by treating dilute lead nitrate solution (1 : 150) with sodium arsenate solution (1 : 10), the precipitate being filtered off, washed, pressed, dried and powdered (U.S. Pat. 1,064,639, 1913).

FIFTH GROUP

BISMUTH: Bi, 208

This element is a member of the same group in the periodic system as arsenic and antimony, but on account of its high atomic weight it has no non-metallic characters and may be considered as a metal, as it forms no gaseous hydrogen derivative and its oxide has basic characteristics.

Bismuth is found naturally both in the pure state and as *Bismuthine*, Bi_2S_3, and in the form of oxide. In order to extract the bismuth the ores are first roasted and then smelted with addition of iron, which acts as a desulphurising agent, of fluxes to eliminate the gangue, and of carbon to reduce the oxide to metal. The bismuth is then freed from traces of other less fusible metals, such as Ni, Co, Ag, Pb, Fe, by liquation, the last traces of impurities being eliminated by allowing the molten bismuth to run over inclined iron plates, during which process the foreign metals are oxidised and eliminated. It is finally melted with KNO_3 or Na_2CO_3 and $KClO_3$.

The pure metal has a lustrous appearance like antimony, but may be distinguished by its reddish reflex. It crystallises readily and is very brittle. It has a specific gravity of 9·8, melts at 267°, and distils at about 1600°. It is not altered in cold air, but on heating it forms the oxide, Bi_2O_3. It is readily soluble in HNO_3, with which it forms the nitrate. It does not dissolve in cold HCl or H_2SO_4, but on heating with H_2SO_4, SO_2 is evolved and the sulphate is formed.

It also combines readily with the halogens. The soluble salts form insoluble basic precipitates when their solutions are diluted with much water, thus behaving similarly to antimony, but basic bismuth salts do not dissolve in tartaric acid.

Bismuth forms *easily fusible alloys* which are suitable for the reproduction of woodcuts, for fusible valves and wires, etc. **Wood's Metal**, consisting of 3 parts of cadmium + 4 of Sn + 8 of Pb + 5 of Bi, melts at 68°; **Rose's Metal**, consisting of 9 parts of Bi + 8 of Pb + 3 of Sn, melts at 79°; **Newton's Alloy** (8 of Bi + 5 of Pb + 3 of Sn) melts at 94·5°; and **Lipowitz's Alloy** (15 of Bi + 8 of Pb + 8 of Sn + 3 of Cd) melts at 70° and softens at 60°.[1]

---

[1] **Theory of the Melting-Point of Alloys.** In the more common alloys the melting-point is usually lower than the arithmetic mean of those of its components. The metals present in a molten alloy often separate on solidification in the form of mixed crystals, or may form true chemical combinations. By the aid of thermodynamics the melting-point of an alloy may be calculated in advance by considering it as a dilute solution, but only in those cases in which the components do not form mixed crystals or undergo chemical combination. In the case, for example, of an alloy consisting mainly of molten tin as solvent, the metals which do not form mixed crystals or chemical compounds are Ag, Pb, Cd, Bi, Zn, Tl, etc. If the alloy consists of 99 atoms of tin (the melting-point and solidifying-point of which is 232°) with 1 atom of another metal, then the lowering of the solidifying point is given by the general formula, $\frac{0{\cdot}02T^2}{Q.M}$, where T indicates the absolute temperature, and Q the latent heat of fusion of tin.

In the case of tin as a solvent, $T = 273 + 232 = 505$, and $Q = 14{\cdot}25$, and the lowering of the melting-point by 1 atom of another metal is 3°. In the case of an alloy prepared in the proportions of 96·2 atoms of tin and 3·8 atoms of silver, the temperature of solidification, that is, the point at which the first crystals of the solvent tin commence to separate, will be $232° - (3 \times 3{\cdot}8) = 220{\cdot}6°$, whilst in practice it is found to be 221°. This rule is, however, only true for concentrations up to about 5 per cent. of dissolved atoms, that is, for dilute solutions. One can understand that as the crystals of the solvent gradually separate, the solution which remains melted is more concentrated, and thus the solidifying point continues to descend until a certain limit is reached. If an alloy is made containing 95·6 atoms of lead (melting-point 328°) with 4·4 atoms of silver, the temperature of solidification or of fusion will theoretically be $328 - (4{\cdot}4 \times 5{\cdot}4) = 304{\cdot}2°$, where 5·4 is the atomic lowering of the melting-point referred to the solvent, lead; in practice the melting-point is found to be 303°. In the case of high concentrations and for ternary alloys, the *eutectic-points*, already studied on pp. 516–517, must be considered, and when true chemical compounds are formed between the metals in the alloy we have well-determined melting-points which are sometimes higher than the melting-points of the components. Thus, an alloy containing 94·5 per cent. of mercury, which melts at − 38·6°, and

By suitably varying the proportions of different metals, alloys of various melting-points may be obtained, so that safety-valves for steam boilers may be prepared, as is shown in the following Table :

Bi	Pb	Zn	Melting-point	Steam pressure	Bi	Pb	Zn	Melting-point	Steam pressure
Parts	Parts	Parts	Degrees	Atmospheres	Parts	Parts	Parts	Degrees	Atmospheres
8	5	3	100	1	8	16	12	146	4
8	8	4	113·3	1½	8	22	24	154	5
8	8	3	123	2	8	32	36	160	6
8	10	8	130	2½	8	32	28	166	7
8	12	8	132	3	8	30	24	172	8
8	19	14	143	3½					

Easily fusible alloys of bismuth cost from 12*s.* to 16*s.* per kilo.

Until 1880 bismuth was produced almost exclusively in Germany and Austria; of late years the greater portion has been produced in Bolivia and Australia. In 1860 the total production of bismuth was 6 tons; it was 40 tons in 1870, 58 tons in 1881, and after this date the Austrian and German production almost entirely ceased, and we find, on the other hand, that in 1907 the United States produced 4 tons and imported 120 tons, of the value of £60,000. Bolivia produced bismuth in 1907 to the value of £140,000. The price was 7*s.* 2*d.* per kilo in 1860, £1 4*s.* in 1870, 16*s.* in 1894, and 10*s.* 5*d.* in 1900; after this the price rose to £1 12*s.* per kilo, a European trust monopolising the American bismuth. Italy produced 500 kilos of *bismuth salts* in 1905, of the value of £400, and 1500 kilos in 1906, of the value of £760; in 1907 Italy imported 5000 kilos and in 1909 3300 kilos, whilst it exported 500 kilos in 1908; in 1914 the output of bismuth salts was 4000 kilos.

BISMUTH CHLORIDE : $BiCl_3$. This compound is obtained by dissolving bismuth in aqua regia or by heating bismuth in chlorine. It forms a white, crystalline mass which melts at 227° and boils at 447°. It is soluble in little water, and is decomposed by much water forming bismuth oxychloride, $BiOCl$, which is a white, amorphous substance insoluble in water, but soluble in acids.

BISMUTH SUBOXIDE : BiO, is probably formed as a dark brown powder on adding an alkaline solution of stannous chloride to a solution of $BiCl_3$.

BISMUTH TRIOXIDE : Bi_2O_3. This is found ready formed in nature and may be prepared by heating the carbonate, nitrate, or hydroxide. It forms a yellowish, insoluble powder of sp. gr. 8·2, which melts at a red heat forming a brown liquid solidifying in a crystalline form.

It is used in the manufacture of crystal glass to replace PbO, as it increases the refractivity. It costs £2 per kilo.

The **DIOXIDE, BiO_2,** is only slightly known and the **PENTOXIDE, Bi_2O_5,** is a brown powder which is obtained from bismuthic acid at 130°; on heating alone or with sulphuric acid it evolves oxygen and when heated with HCl forms chlorine and $BiCl_3$, so that it may be considered rather as a peroxide than as an anhydride.

BISMUTH HYDROXIDES. The **ORTHOHYDROXIDE, $Bi(OH)_3$,** is a white, amorphous powder which has basic properties, and is formed on adding an alkali to a solution of a bismuth salt. It is insoluble in potassium hydroxide and in NH_3 and loses 1 mol. of water at 100°, being transformed into the **Metahydroxide, $BiO \cdot OH$,** which also has basic properties and forms basic salts, whilst the orthohydroxide forms neutral salts.

BISMUTHIC ACID : $HBiO_3$. On electrolysing a mixture of $KOH + KCl + Bi_2O_3$ in the hot, potassium bismuthate, $KBiO_3$, scarlet in colour, is deposited at the anode. At 120° it loses 1 mol. of H_2O and becomes dark; at higher temperatures it becomes black and evolves oxygen. At 300° it suddenly acquires a brick-red colour, the substance which is formed being an allotropic form of Bi_2O_3.

BISMUTH NITRATE : $Bi(NO_3)_3$. This is obtained crystallised with $5H_2O$ when bismuth is dissolved in nitric acid and the solution then evaporated. It is easily soluble

---

5·5 per cent. of sodium, which melts at 97·5°, has a melting-point of 360°, but in this case we have a true chemical combination, $NaHg_2$. Further, a mixture of Hg and $NaHg_4$ containing 99·1 per cent. of Hg and 0·9 per cent. of Na has a solidifying-point of $-48·2°$, which is thus lower than that of pure mercury.

in a little water, especially in presence of HNO_3, whilst with much water (20 parts) a stable basic bismuth nitrate separates on heating, which is known as the **Subnitrate** or as *Magister of Bismuth*, $Bi(NO_3)_2OH + BiNO_3(OH)_2$. This is used medicinally and also in the preparation of cosmetics, but since it becomes yellow in the air and blackens with H_2S, it is being more and more replaced as a cosmetic by zinc oxide which has not these disadvantages. *Italy* produced 4 tons (£4000) of bismuth nitrate in 1916.

On dissolving bismuth in H_2SO_4 the **Neutral Sulphate, $Bi_2(SO_4)_3$**, and the **Basic Sulphate, $Bi_2SO_4(OH)_4$**, are formed.

BISMUTH SULPHIDE : Bi_2S_3. This is found in nature as *Bismuthine*, but is also prepared artificially by melting sulphur with bismuth or from a solution of a bismuth salt with H_2S, and then forms a black powder insoluble in water, but soluble in hot dilute HNO_3. It is insoluble in alkali sulphides, because it does not form sulpho-salts in the same manner as As and Sb. A disulphide, Bi_2S_2, is also known, consisting of grey crystals which are obtained on melting the two components together.

SIXTH GROUP

This includes four elements, **Chromium, Cr** (atomic weight 52); **Molybdenum, Mo**, 96; **Tungsten, W**, 184; and **Uranium, U**, 238·5. The compounds of these metals have certain analogies with those of sulphur, especially in the case of the higher oxides, and just as there is sulphuric anhydride, SO_3, so we also have the oxides, CrO_3, MoO_3, WO_3, and UO_3, which have acid characters and should be considered as true acid anhydrides. The salts have an analogous constitution to the sulphates and are isomeric with them. The strength of these acids diminishes with increase of the atomic weight. The sesquioxides of this group, such as Cr_2O_3, have basic characters and present many analogies with those of Fe, Mn, and Al.

CHROMIUM: Cr, 52

This element is found in nature, especially as **Chrome Iron Ore, FeO,Cr_2O_3**, or *chromite*, and in smaller quantity as *crocoite*, $PbCrO_4$. Pure chromium was first obtained by Moissan in 1894 by reducing Cr_2O_3 with carbon in the electric furnace, but it is still more easily obtained in the pure state to-day by the alumino-thermic process (Goldschmidt, p. 727), by reducing chromium oxide with aluminium powder : $Cr_2O_3 + Al_2 = Al_2O_3 + Cr_2$.

The chromium obtained in the past always contained carbon and was not suited to the manufacture of chrome steel. Pure chromium is a grey shining metal which does not alter in the air. It has a specific gravity of 6·8, and melts only at 1520°. Chromium prepared by the Goldschmidt process behaves as a *passive* metal, that is, it is not attacked by dilute cold HCl or H_2SO_4, or by HNO_3, even on heating. Chromium obtained in any other manner is very *active*, that is, it evolves H even in the cold with these acids. The other form also becomes active when it is heated with alkalis, dilute acids or solutions of NH_4Cl, so that it may also be used as the cathode of a cell. The E.M.F. of inactive chromium (p. 523) is 0·3 volt, whilst that of active chromium is 1·8 volt. It seems that the passivity of metals is due to a layer of oxygen which covers the outer surface of the metal, and a metal may even become passive in the air, but more easily by the action of HNO_3, $FeCl_3$, H_2O_2, or by employing it as an anode in solutions of KF, KCN, and chromic acid. The following metals may assume the passive state: Fe, Ni, Co, Cr, Mo, W, V, Ru. Nowadays the view prevails that these metals in the very pure state are passive and that they become active under the catalytic action of hydrogen ions; the phenomenon of passivity is not, however, fully explained.

Small additions of chromium to certain other metals render them harder and more resistant to various chemical reagents. Before 1898 chromium cost more than £60 per kilo, but since the introduction of the Goldschmidt process the price has gradually fallen to 8*s*. per kilo.

Chromium forms four series of compounds which may be considered to be derived from chromous oxide, CrO, chromic oxide, Cr_2O_3, chromic acid, and perchromic acid respectively. All these compounds have coloured ions.

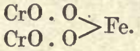
The **CHROMOUS COMPOUNDS** are the least stable and are obtained by the reduction of chromic compounds, but are very easily oxidised by the air. Thus **Chromous Chloride,** $CrCl_2$, is obtained from Cr and HCl or by reducing chromic chloride, $CrCl_3$, with nascent hydrogen, in the form of a white, crystalline powder forming a blue solution which rapidly absorbs oxygen from the air, during which process its colour is changed to green. Its vapour density at 1600° corresponds with a mixture of $CrCl_2$ and Cr_2Cl_4.

CHROMOUS HYDROXIDE : $Cr(OH)_2$. This is obtained as a yellow precipitate by adding an alkali to a solution of $CrCl_2$.

Chromous salts differ from the chromic salts by forming black **Chromous Sulphide,** CrS, with alkali sulphides.

CHROMIC OXIDE : Cr_2O_3. This is obtained as a green powder by heating ammonium dichromate or chromic anhydride, CrO_3, to redness. When melted with silicates it forms beautiful green-coloured glasses and porcelains. When 1 part of potassium dichromate is melted with 3 parts of boric acid and the potassium borate then dissolved in water, a beautiful green pigment remains, which is known as *Guignet's green*, or *chrome green*, and is a hydrate of chromic oxide, $Cr_2O(OH)_4$. Italy produced 70 tons of this product in 1905, 100 tons in 1907, of the value of £1800, and 70 tons in 1908, of the value of £420 (?).

CHROMIUM HYDROXIDE : $Cr(OH)_3$. This compound is formed as a gelatinous bluish-grey mass on adding NH_3 to solutions of chromic salts; it dissolves in NaOH to form a green solution which deposits the hydroxide on boiling. It is clear from this reaction that the hydroxide has feebly acid characters and forms with strong bases unstable salts which are derivatives of the metahydroxide, CrO·OH, and analogous to the *spinels* which are obtained from Al. These compounds are called *chromites*, so that natural *chrome iron ore* is a chromite of iron :



$$\begin{matrix} CrO\,.\,O \\ CrO\,.\,O \end{matrix}\!>\!Fe.$$

Chromium hydroxide acts as a very weak base and forms salts only with strong acids and not with carbonic acid; thus sodium carbonate precipitates the hydroxide and not the carbonate from chromium salts (p. 733).

CHROMIUM CHLORIDE : $CrCl_3$. This is formed on passing a current of chlorine over heated chromium or over a mixture of Cr_2O_3 and charcoal, and sublimes in lustrous violet crystals. Its vapour density at 1300° corresponds with the formula $CrCl_3$. It is only slightly soluble in water even on heating, but becomes readily soluble in presence of a trace of $CrCl_2$, which acts catalytically, forming a green liquid which deposits green crystals, $CrCl_3,6H_2O$, on concentration, similar to those obtained from a solution of $Cr(OH)_3$ in HCl, whilst on dissolving the hydroxide in HCl a basic chloride is formed. Both are used as mordants in calico printing.

CHROMIUM FLUORIDE : $CrF_3 + 4H_2O$. This compound forms a bright green crystalline powder, stable in the air, and readily soluble in water. It is used as a mordant for various alizarin dyestuffs on wool and costs about £60 per ton.

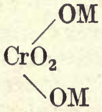
CHROMIUM SULPHATE : $Cr_2(SO_4)_3$. This is obtained on dissolving the hydroxide, $Cr(OH)_3$, in sulphuric acid. The cold aqueous solution has a violet colour, but becomes green on heating to 80°. On cooling, the violet colour reappears. Violet-blue crystals containing $16H_2O$ may be obtained from this solution, but on evaporating this green solution a green amorphous residue remains. In the green solution the simple chromium ions are no longer present, but only a more complex ion; for this reason the green solution does not give the ordinary reactions for chromium salts.

CHROME ALUM : $Cr_2(SO_4)_3,K_2SO_4 + 24H_2O$. This may be prepared in the manner common to all the alums by mixing potassium sulphate with the sulphate of the heavy metal, or more easily by passing SO_2 into a solution of potassium dichromate in presence of H_2SO_4: $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = H_2O + Cr_2(SO_4)_3,K_2SO_4$.

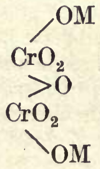
From this solution the alum may be obtained in very large octahedra of a bright violet colour. This alum also forms in the cold a violet solution which becomes green on heating to 80° and regains its violet colour on cooling (*see above*).

DERIVATIVES OF CHROMIC ACID

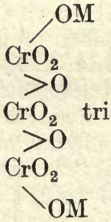
As we have already said, the analogy between chromium and sulphur is manifested especially in the derivatives of chromic acid, but whilst chromic anhydride, CrO_3, corresponding with sulphuric anhydride, is well known, chromic acid, H_2CrO_4, corresponding with H_2SO_4, is not known in the free state, although the corresponding salts, namely, the chromates, which are isomorphous with the sulphates, are well known and have been largely studied. Salts corresponding with polychromic acids are also known, such as the dichromates, trichromates, etc., and are represented by the following constitutional formulæ, where M indicates a monovalent metal and where the one formula is derived from the other by the addition of one molecule of CrO_3 :



chromates;



dichromates;



trichromates, etc.

The chromates are yellow and the corresponding acid salts are not known. By the action of acids chromates are transformed into dichromates or polychromates, which have a reddish-orange colour, whilst on the contrary polychromates are reconverted by alkalis into chromates, as can easily be seen by the change of colour of the solutions. Chromic acid is a weak acid and its insoluble barium, silver, and other salts are dissolved by strong acids.

CHROMIC ANHYDRIDE : CrO_3 (Chromium Trioxide). This compound is obtained in the form of lustrous red needles by the action of H_2SO_4 on a concentrated solution of potassium or sodium dichromate :

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

It is easily soluble in water, and when the crystals are pure they are not deliquescent. When heated to 250° it becomes brown, melts, and decomposes, forming oxygen and chromic oxide, $2CrO_3 = Cr_2O_3 + O_3$. It is such an energetic oxidising agent that it sets fire to alcohol when brought into contact with it, and its solution cannot be filtered through filter-paper because the latter is destroyed: thus, it behaves in a very similar manner to a peroxide, evolving oxygen and being transformed into chromic oxide.

ALKALI CHROMATES and DICHROMATES, Na_2CrO_4 and $Na_2Cr_2O_7$. The alkali chromates are obtained by melting a chromium compound with an alkali carbonate in presence of an oxidising agent such as a nitrate or atmospheric air. Industrially, chrome iron ore is melted in a reverberatory furnace with soda and lime in presence of air :

$$2Cr_2O_4Fe + 4Na_2CO_3 + 4CaO + 7O = Fe_2O_3 + 4CaCO_3 + 4CrO_4Na_2;$$

or a mixture of 25 parts of chromite, 10 of sodium sulphate, 8 of NaCl and 25 of calcium hydroxide is treated with superheated steam at about 700°. The addition of lime saves alkali hydroxide or carbonate and also prevents the mass from fusing, so that it remains porous and more easily oxidisable by the air. If potassium chromate is desired, the Na_2CO_3 and CaO are replaced by powdered calcium hydroxide moistened with potassium carbonate solution, the green mass being afterwards extracted with hot saturated potassium sulphate solution, which transforms also the calcium chromate into potassium chromate.

The melt thus formed, which contains sodium chromate mixed with calcium chromate (*see also* U.S. Pat. 994,129, 1911), is dissolved in water and a little Na_2CO_3, and the solution then decanted and concentrated, after acidification with acetic acid, until crystallisation commences. If crystallisation occurs below 30°, crystals with $10H_2O$, isomorphous with Glauber's salt, are obtained; these melt even with the heat of the hand and are very hygroscopic and effloresce in the air. The lemon-yellow crystals, which contain no water of crystallisation, are very soluble in water and insoluble in alcohol and show an alkaline reaction. If sodium dichromate, $Na_2Cr_2O_7 + 2H_2O$, is required instead of the chromate, the above-mentioned solution is slightly acidified with sulphuric acid and evaporated until it crystallises.[1] Sodium dichromate is hygroscopic and very soluble in water. In order to obtain **Potassium Dichromate** it suffices to heat the solution of the sodium salt with KCl, when after concentration NaCl readily separates on the bottom of the vessel and $K_2Cr_2O_7$ forms in very fine triclinic crystals on leaden rods suspended in the liquid. These crystals are of an orange-red colour, contain no water of crystallisation, and are not hygroscopic. The compound is somewhat poisonous, has the sp. gr. 2·69, and melts unchanged below a dull red heat, although at white heat it evolves oxygen and yields chromium oxide and potassium chromate.

The solubility of potassium chromate and dichromate in 100 parts of water at different temperatures is :

	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Chromate .	58·9	60·9	62·9	64·9	67	69	71	73	75	77	79
Dichromate .	4·6	7·4	12·4	18·4	25·9	35	45	56·7	68·6	81	94

Its oxidising action, especially on heating in presence of H_2SO_4, is shown by the following equation :

$$K_2Cr_2O_7 + 4H_2SO_4 = 4H_2O + Cr_2(SO_4)_3, + K_2SO_4 + 3O,$$

which consists in the transformation of the chromic anhydride (of chromic acid) into green oxide of chromium (soluble in acids) : $2CrO_3 = Cr_2O_3 + O_3$. The oxidation of a ferrous salt to a ferric salt by dichromate in presence of acid is explained by the equation :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

The chrome alum thus produced, and all reduced chromium salts from various chemical reactions, may be re-utilised by submitting them to electrolysis with lead electrodes separated by diaphragms. During the passage of the current chromic acid forms in the anodic space and can be again used as an oxidising agent, whilst H is evolved at the cathode.[2]

---

[1] In an Austrian sodium dichromate works the finely ground chromite is mixed with powdered quicklime and less than the theoretical quantity of sodium carbonate, the mixture being heated, in a furnace with three floors arranged stepwise, by gas from a generator supplied with air heated by the waste furnace gases. On the first hearth the temperature reaches 900° to 1000° and the mass is mixed several times during 4 to 5 hours without fusing at any point; the coal consumption is about 180 kilos per 100 kilos of ore. Furnaces with revolving hearths (p. 595) are also used, but the consumption of coal is similar. The mass from the furnace is dissolved in a little water and the remaining quantity of sodium carbonate, and is stirred under pressure in an autoclave and then passed through a filter-press, the residue being well washed on the filter so that the cakes to be discarded do not contain more than 1 per cent. CrO_3. The solution is concentrated and discharged into lead-lined vessels, where the sulphuric acid necessary to transform the chromate into dichromate is added, a minimal quantity of chromate being, however, left to prevent attack of the succeeding concentration vessels by the solution after the separation of the anhydrous sodium sulphate (this is centrifuged and washed until it contains less than 1 per cent. of CrO_3). The concentration is carried out in cast-iron vessels furnished with stirrers, which scrape the bottom and sides so as to prevent formation of crusts of sulphate crystals. When the sp. gr. reaches 66° Bé. the mass is filtered and the solution allowed to crystallise in iron vessels. The crystals are centrifuged and packed while still hot, owing to their hygroscopic character. In some cases the ore is fused with NaOH at 500°.

[2] **Recovery of the Chromium.** Where dichromate is used to effect oxidation, especially of organic matter in waste liquors, the chromium is left as sesquioxide, usually as chromium sulphate in presence of excess of chromium. The latter may be recovered by transforming it into dichromate in various ways : (1) *By calcination.* The boiling acid liquid is treated with the calculated quantity of lime to precipitate all the free and combined sulphuric acid as calcium sulphate, then left to settle and the clear liquid decanted off, treated with a further calculated quantity of lime to precipitate all the chromium as hydrated chromic oxide and finally with sufficient lime to form calcium chromate : $Cr_2(SO_4)_3 + H_2SO_4 + 4Ca(OH)_2 = Cr_2(OH)_6 + 2H_2O + 4CaSO_4$ and $Cr_2(OH)_6 + 2CaO + 3O = 2CaCrO_4 + 3H_2O$. The last phase of the reaction is effected in three cylindrical calcination furnaces, revolving so that the pasty mass charged into one cylinder passes into the second and then into the third, which is the nearest to the furnace giving the hot gases and oxygen. In its passage from one cylinder to another, the paste assumes the form of balls (2 to 4 cm. in diameter) of yellow calcium chromate, which are partly broken up and powdered when they leave the hottest cylinder; a dull red hea suffices. The product obtained is finely powdered, made into a paste with sodium sulphate or bisulphate solution, heated in a suitable vessel, mixed to a pulp with water, and filtered to remove

Dissolution of potassium dichromate in more or less dilute nitric acid and subsequent crystallisation yield, according to the conditions, *potassium nitrodichromate*, $Cr_2O_5(OK)(NO_2)$, or *potassium nitrotrichromate*, $Cr_3O_8(OK)(NO_2)$, or *potassium tri-* or *tetra-chromate*, $Cr_4O_{11}(OK)_2$.

USES.—Potassium and sodium dichromates are used in large quantities as mordants in dyeing wool with alizarin dyestuffs or logwood black (*see* Vol. II., " Organic Chemistry ") and in printing textiles; also as oxidising agents in making various organic compounds, in bleaching fats, and with the help of sunlight to render gelatine insoluble for photographic or polygraphic purposes; they are employed also in tanning hides, making fireworks, etc.

STATISTICS AND PRICES. The principal works manufacturing potassium dichromate are in England, which country has almost a monopoly of this product; the prices have now fallen, however, because in Germany works have arisen which manufacture **Sodium Dichromate**, which is less expensive and can almost always be used instead of the potassium salt, which costs about £30 per ton, whilst sodium dichromate costs about £22.

Commercial potassium dichromate should have a purity of 98 to 99·5 per cent. (67 to 68 per cent. of CrO_3), and the sodium salt should contain at least 74 per cent. of CrO_3.

The amounts (tons) of potassium (K) and sodium (Na) dichromates produced, etc., in *Italy* are as follows:

		1905	1908	1910	1912	1913	1914	1915	1916	1917
Production	K	300	200	342	386	529	450	531	—	—
	Na	610	600	476	422	794	574	448	—	—
Importation, K + Na		400 ?	291	68	72	6	3	901	436	447
Exportation, K + Na		200 ?	297	1	10	—	70	2	—	—

In 1909 *England* exported 4700 tons of sodium and potassium dichromates, in 1910 5800, and in 1911 4300 tons.

Germany produced about 3000 tons of dichromate in 1908.

Chromates of various other metals are also known, and are used as pigments or for other purposes. **Lead Chromate, $PbCrO_4$,** is much used as a pigment under the name of *chrome yellow*, which is obtained from a soluble lead salt, such as the acetate, with sodium or potassium chromate. On heating, it is a strong oxidising agent for organic substances. **Chrome Red** is a basic lead chromate, $PbCrO_4,Pb(OH)_2$. **Barium Chromate, $BaCrO_4$,** is used as a mineral pigment which is very resistant to atmospheric influences, etc. Many chromates crystallise with $7H_2O$ and are isomorphous with magnesium sulphate.

AMMONIUM DICHROMATE, $(NH_4)_2Cr_2O_7$, forms fine garnet-orange crystals soluble in water. When heated strongly at one point it ignites and then continues to burn alone, leaving a light voluminous residue of Cr_2O_3. It costs £110 per ton. It is obtained by semineutralisation of chromic acid solution, followed by concentration and crystallisation.

On distilling a dichromate with NaCl and H_2SO_4, a blood-red liquid distils over of sp. gr. 1·96, which boils at 117°, and consists of **Chromium Oxychloride** or **Chromyl Chloride, CrO_2Cl_2.** It is decomposed by water, forming HCl and CrO_3. A **Monopotassium Chromyl Chloride, CrO_2ClOK,** is also known.

PERCHROMIC ACID. On treating a minimal quantity of a dichromate or chromate with H_2SO_4 and a little hydrogen peroxide, a blue coloration is formed, and on shaking the liquid with ether (washed and free from alcohol, as it might contain traces of H_2O_2), the colour passes into the ether and then rapidly disappears. This is probably due to **Perchromic Acid, $HCrO_5$,** which cannot be isolated, but of which an ammonium salt,

---

the gypsum: $2CaCrO_4 + 2NaHSO_4 = 2CaSO_4 + H_2O + Na_2Cr_2O_7$; the dichromate solution is either concentrated in the manner already described to cause it to crystallise, or used as it is for the oxidation process. (2) *By electrolysis.* According to Ger. Pats. 103,860, 117,949, 138,441, 182,287, 199,248, and 251,694, continuous electrolysis may be carried out without diaphragms by separating the cathodic from the anodic zone by partitions which do not reach the bottom of the vessel, the supply of liquid being regulated so as to maintain a constant acidity at the anode. In this way 90 per cent. of the current is utilised, about 500 kilowatt hours at 3 to 6 volts being consumed to regenerate 200 kilos of dichromate. The electrolytic process requires no separation of the sulphuric acid and economises the amount of acid necessary to convert the chromate into dichromate.

$NH_4CrO_5 + H_2O$, and a corresponding **Anhydride, Cr_2O_9**, which acts as a peroxide, are known. This reaction with the blue coloration is very sensitive and is used for the detection of traces of chromic acid or of hydrogen peroxide.

CHROME ALUM, $CrK(SO_4)_2 + 12H_2O$ (*see* pp. 116 and 797) forms fine, brownish-violet crystals, giving a reddish-violet aqueous solution. It serves as a mordant in dyeing, and in the chrome tanning of hides. When boiled with NaOH, the aqueous solution gives a green precipitate.

It is prepared by reducing dichromate solution acidified with sulphuric acid by means of sulphur dioxide, or by saturation with SO_2 in the cold of a chromium sulphate solution of about 30° Bé. mixed with the calculated quantity of K_2SO_4; in a short time large crystals separate, while further saturation of the mother-liquors yields minute crystals of an amethyst colour (J. Hertkorn, Ger. Pat. 265,046, 1912).

Chrome alum costs £20 to £22 per ton.

MOLYBDENUM: Mo, 69

This is found somewhat rarely in nature in *wulfenite*, $PbMoO_4$, but more frequently as *molybdenite*, MoS_2, which is roasted, and the oxide MoO_3, thus formed, heated in a current of hydrogen or with charcoal in the electric furnace in order to obtain metallic molybdenum. When thus prepared it is a grey powder which at extremely high temperatures forms a fused mass of silvery appearance and sp. gr. 8·6. When heated in the air it first forms MoO_2 and then MoO_3. It dissolves in concentrated HNO_3 or H_2SO_4.

In the electric furnace with excess of carbon it forms **Molybdenum Carbide, Mo_2C.**

Molybdenum forms numerous compounds in which it exercises the most varied valencies (from 2 to 8). Thus various chlorides, $MoCl_2$, $MoCl_4$, $MoCl_5$, are known and also the oxychlorides, $MoOCl_4$, MoO_2Cl_2, etc. Of the various oxides, Mo_2O_3, MoO_2, and MoO_3, the last is the most important and possesses acid characters, whilst the first is a weak base and the second is neutral. **Molybdic Anhydride, MoO_3,** is insoluble in acids and in water, but dissolves in sodium hydroxide or in NH_3. It is a white substance which becomes yellow on heating, similarly to ZnO.

It forms polyacid salts, $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, etc. One of the commonest and most stable of these salts is **Ammonium Heptamolybdate, $(NH_3)_6Mo_7O_{24},4H_2O$,** commonly known as **Ammonium Molybdate.** This is soluble in an excess of nitric acid and its solution is a good reagent for the quantitative precipitation of phosphoric acid from soluble phosphates on warming in the form of yellow crystals of the composition $11MoO_3, PO_4(NH_4)_3$. A similar precipitate is produced with arsenates.

In order to detect traces of molybdenum the solution is treated with zinc and H_2SO_4, when a blue coloration is first formed, which gradually becomes brown, the former coloration being due to Mo_3O_4, and the latter to Mo_2O_3.

TUNGSTEN: W, 184 (In German, Wolfram)

This element is found in nature in certain minerals, which are utilised especially in the United States, Australia, Canada, Spain, Portugal, England, etc.; the most important are *wolframite*, $FeO(MnO)WO_3$ (*see* note), *scheelite*, $CaWO_4$, *hübnerite*, $MnWO_4$ (with 72 to 77 per cent. WO_3), *stolzite* (lead tungstate), *ferberite* (mostly iron tungstate), *cuproscheelite*, *powellite*, *raspite*, *megabasite*, etc.[1]

---

[1] Of the various ores the most abundant is *wolframite*, a ferro-manganous tungstate, $FeO(MnO)WO_3$, which forms lamellar masses or voluminous, shining crystals of a deep grey colour, sp. gr. 7·2 to 7·5 and hardness 5·5. With aqua regia it leaves an insoluble, yellow, pulverulent residue of *tungstic acid*, whilst with hot concentrated HCl it forms a colourless liquid, turned blue by zinc. Commercial wolframite, screened at the mine, is sold as concentrated ore of the strength 50 to 65 per cent. (standard, 60 per cent.) of tungstic acid, WO_3, or as first quality with 68 to 70 per cent. WO_3, which should be free from injurious elements, such as Sn, Sb, As, S and Cu. A sample of commercial wolframite gave the following percentage composition: WO_3, 64·13; FeO, 10·88; Al_2O_3, 5·32; MnO, 6·42; SnO_2, 0·68; MgO, 3·16; CaO, 1·21 and SiO_2, 7·71.

Scheelite is more difficult to work industrially. It occurs in octahedral crystals or in compact or granular, shining, translucent masses, colourless, yellowish or brown. Its density is 5·9 to

To obtain tungsten or its oxides, the ore is finely ground after screening and passing over magnets (*see* footnote), the quartz being separated by levigation with water, from which the purified tungsten ore is best deposited by addition of lime water.

The free metal is obtained by Goldschmidt's thermit process, the tungstic acid being reduced by powdered aluminium (*see* p. 727), but, according to Watt, a flux (fluorspar or cryolite) is necessary; in an electric furnace taking 600 amps. at 80 volts the operation is complete in five minutes.

According to U.S. Pats. 964,868–964,871, tungsten sufficiently pure for making tungsten steels is obtained by heating wolframite or scheelite in earthenware pipes at 90° with substances which liberate chlorine and hydrochloric acid. The Ca, Mn and Fe, thus rendered soluble, are eliminated and the residual tungstic acid mixed with silica is reduced at 1000° in presence of carbonaceous material, and the crude tungsten thus formed used directly for steels. During recent years many processes for preparing tungsten have been patented.

Ore containing tin is melted in a reverberatory furnace with sodium sulphate, coke and oxide of iron, the sodium tungstate being then separated by means of water from the crude tin. The tungstate solution is concentrated, allowed to crystallise, and filtered, the little tin dissolved in the filtrate being precipitated by means of CO_2. The powdered ore may also be treated with an equal quantity of HCl at 20° Bé., heated to 90° and oxidised with 1 per cent. of sodium chlorate; steam is passed through for 15 to 18 hours, the liquid then decanted off and the residue (WO_3 and SiO_2) treated with ammonia and fused directly in the crucible with the steel. For reduction of the ore with coal and direct use of the product for crucible steel, *see* Ger. Pat. 246,386, 1910. A. H. Perret (Ger. Pat. 264,373, 1910, and 265,769, 1913) treats the ores (especially those with vanadium) with concentrated sodium hydroxide and carbonate solution, the dissolved silica being separated from the product by an aluminium salt and the liquid filtered hot, and the tungstic or vanadic acid precipitated by means of sulphuric acid.

According to Ger. Pat. 247,993, 1911, fused metallic tungsten almost free from carbon may be obtained by heating tungstic acid in an electric furnace at 2800° to 2900° with less than the theoretical quantity of calcium carbide and a little ferrosilicon : $WO_3 + CaC_2 = W + CaO + 2CO$; the slag floats on the fused metal, preserving it from the carbon, and the last traces of this are eliminated by the CaO, which is converted into carbide.

6·1 and its hardness almost 5. With boiling HCl, it leaves a yellow powder soluble in ammonia. A sample of the concentrated ore contained 77·84 per cent. WO_3, 19·48 per cent. CaO, and 2·23 per cent. MoO_3.

Ores used for making ferrotungsten for steel should be freed from sulphur and phosphorus by means of electrical separators which lower the sulphur from, say, 6 to 0·4 per cent., and after roasting to 0·08 per cent.

Before tungsten was used for steel and for electric lamps, *Australia* exported 275 tons (1899) of concentrated tungsten ore, whilst in 1904 Queensland alone exported 1525 tons, this overproduction diminishing the exportation in succeeding years; later, however, more was exported, the amount in 1910 being 1520 tons. *England* produced 182 tons of tungsten ore in 1913 and 205 tons (£19,720) in 1914. In the *United States* tungsten ores are comparatively abundant in Colorado, Arizona, Utah, California (480 tons in 1910), and Montana. North America produced about 1540 tons of ore in 1910 (540 tons with 35 per cent., and 1000 tons with 60 per cent. WO_3), 1125 in 1911, 1250 in 1912, and 1400 in 1913. Further, the *Argentine* yielded 300 tons of ore in 1908, and tungsten also abounds in *Brazil*. *S. America* gave 1080 tons of the ore in 1910. *British India* also contains tungsten ore (near Nagpur). In *Japan* tungsten minerals were found a few years ago in the Outake mountains (Yamanaski). *Spain* (at Caceres, Cordova, Salamanca, Galicia, Coruna, Pontevedra, etc.) in 1905 produced 900 tons, and in 1910 300 tons of the ore. Tungsten ore is found also in *Portugal* (at Tras-os-Montes, Castello Branco and Pinkel), and the output in 1910 was 1200 tons. *Germany* produced only 34 tons (at Altenberg) and imported 2500 tons, in 1908. *Austria* produces about 50 tons. In *England* (Cornwall) 480 tons of the ore were produced in 1910, 1000 tons being imported. For the first time in 1916, *Italy* produced 7·5 tons of tungsten ore together with stibnite (worth £160 per ton) in Sardinia (at Orroli); it seems that similar ore occurs also in Piedmont on the borders of Liguria. The *world's output* in 1910 was 7200 tons of rich ore, distributed thus : *Asia* (Himalaya, French Indo-China, India), 150 tons; *Australia*, 2000 tons; *Europe*, 1600 tons (54 in Austria, 307 in England, 105 in Germany, 1130 in Portugal); *North America*, 1900 tons; *South America*, 1300 tons (Bolivia gave 210 tons in 1910 and 472 in 1912).

Ch. M. Johnson's process consists in reducing the oxide in a muffle at 1000° with wood charcoal (*see* Ger. Pat. 246,182, 1910).

Electrolytically tungsten is obtained (according to Ger. Pat. 239,877, 1910) with a solution of WCl_6 or WF_6 in acetone, the anodes being of charcoal or graphite and the cathodes of Pt, Ni, Cu, C, etc.; care must be taken that the anodic chlorine does not attack the cathodes. Beckmann effects continuous electrolysis at 1000° of a fused mixture of tungstic oxide (the same holds for vanadium and molybdenum oxides) and lime in equal proportions; tungsten separates at the cathode, whilst oxygen is liberated in abundance at the anode.

According to Ger. Pat. 261,819 of 1911, tungsten oxide is reduced at 500° to 600° by hydrogen at a pressure of 80 atmos. Pure tungsten is obtained by reducing with metallic calcium in a vacuum (Fr. Pat. 419,043, 1909, not taken out in Germany) or with H in presence of P_2O_5 vapour. In the latter case crystallised 99·9 per cent. tungsten is obtained (H. C. Fischer, 1912; also Eng. Pat. 23,475), the operation being carried out in crucibles lined with powdered tungsten so that the metal may not be contaminated.

PROPERTIES. Tungsten has the appearance of lustrous steel, is very hard (scratches glass), melts at 3000°, has sp. gr. 18·7 (powder, about 16·5) and the specific heat 0·035. When it contains a little carbon its hardness approaches that of the diamond. It withstands the action of the air, but in the hot burns with formation of the trioxide, WO_3 (yellow powder); it resists moderately well ordinary reagents and dilute acids, and only a mixture of HF and HNO_3 dissolves it readily. Nitric acid and aqua regia transform it into trioxide. It dissolves in pure caustic potash with evolution of hydrogen.

USES. From its high specific gravity, various uses might be predicted for it, *e. g.*, the preparation of small projectiles, admitting of the use of smaller guns.

Even in small proportion, tungsten imparts special properties to metals and alloys. Since the year 1900 tungsten has been largely employed in making very hard steels. The specific magnetic moment of a tungsten steel is 62, the values for diamond steel, Martin steel and Bessemer steel being 37, 5 and 3 respectively.

The high melting-point has led to the use (since 1903) of tungsten in making the filaments of incandescent electric lamps; 1 kilo of tungsten gives filaments for 50,000 to 60,000 lamps, the thickness being only 0·02 mm.

The great advantage in this use of tungsten is based on the following considerations: the yield of light (*i. e.*, the ratio—very small—between the light rays with small wave-length and the heat rays with longer wave-length) is proportional to the twelfth power of the temperature, and tungsten filaments may be heated to 2500° without melting or subliming, thus giving a luminous efficiency greater than carbon filaments, which sublime considerably at 1500°. Further, a tungsten lamp consumes 1·1 to 1·2 watt per candle-power, carbon filaments consuming 3·5. The success of the tungsten lamp compared with those of osmium and tantalum is similarly explained. In 1911 about 100 millions of such lamps were made. Tungsten oxidises more difficultly than titanium and tantalum during the drawing of the filament, and in any case the oxide at different points may be reduced by means of hydrogen with formation of the hydride—as happens with tantalum and titanium—which lowers the vacuum of the lamp owing to liberation of hydrogen from the hydride in the hot.

Siemens and Halske prepare the filaments of Wotan lamps by drawing out rods of a nickel-tungsten alloy (80 per cent. W) heated electrically at 1400°, hundreds of miles of slender thread being thus formed and then wound on spools. Expert workers hook the filament to the supports of the lamp, which is situate in a vacuum bell, the filament being then heated to 2600° by a current so that all the nickel evaporates. The remaining pure tungsten filament, which has little ductility, is then placed in its lamp, the latter being evacuated. Without the ductile nickel-tungsten alloy, it would be impossible to obtain so thin a tungsten filament. Some works make a paste of very fine tungsten powder with a mastic (tragacanth or celloidin dissolved in amyl acetate) and force the paste under pressure through the imperceptible orifice of a diamond, the mastic being afterwards burnt away; in this way, however, a little tungsten carbide may be formed, this producing irregular resistance in the filament.

In other works colloidal tungsten is drawn out, this being obtained, *e. g.*, by the Kuzel process (Austrian Pat. 29,839, 1904, and Fr. Pat. 371,799), in which powdered tungsten is treated alternately with acid and alkali until a colloidal solution is formed. This is precipitated as a plastic gel, which is made into a paste with ordinary tungsten powder and forced through orifices in a diamond, to obtain the slender filaments. This process was applied in 1908 in the large works of J. Pintsch, but after about £20,000 had been paid to the inventor in 1910 and many thousands of pounds had been lost, it was abandoned, since the filaments were not sufficiently uniform. It was modified by the addition of a small quantity of thorium oxide, organic matter being avoided, as this leaves residues of carbon and carbide, which are deleterious to the homogeneous resistance of the fibre and to the economic use of the electrical energy.

In America ductile tungsten threads are obtained by W. H. Dayton's hammering process (U.S. Pat. 515,576). Small square-sectioned rods, formed of compressed powdered tungsten, are heated to 1000° in a current of hydrogen for an hour, then electrically at 2850°—to incipient softening—after which they are hammered longitudinally (at 1200° to 1300°) at all points by means of a machine giving 6000 blows per minute, the rod being kept in the hydrogen and revolving meanwhile. The heating and hammering are alternated until the diameter is reduced to 1 mm. (from 6 mm.), about 50 hammerings being necessary. The rod is then drawn at 500° to 600° through diamonds with orifices continually diminishing (as many as 16 moulds are used), the end of the rod being pointed by immersion in fused potassium nitrite. Ductile tungsten is sometimes prepared by adding to the tungsten paste thorium salts in amount corresponding with 2 to 5 per cent. of thorium oxide (ThO_2), the filaments then remaining ductile even when the lamp is in use.

Tungsten bronzes are now made by reducing alkali tungstates either with hydrogen or with an electric current or by fusion with tin. Those derived from sodium tungstate have metallic lustre and are golden yellow, red or blue, whilst those from potassium tungstate are deep blue or copper red.

STATISTICS AND PRICES. The *world's production of tungsten ore* (with an average of 60 per cent. WO_3) was about 3600 tons in 1905, 4000 in 1908, 7200 in 1910, and 8000 in 1912. The output in different countries is shown in the note on p. 800; attention may be called to the increased production in Spain, this amounting to 5113 tons (£8733) in 1915 and 4547 (£36,595) in 1916. The amount of tungsten in various degrees of purity produced in 1912 was about 3500 tons, besides about 1000 tons of tungstic acid and different salts. Commercial tungsten has a purity of 93 to 98 per cent., the impurities being C, Mn, Fe, Si and S. The *ferrotungsten* used directly in making steel contains from 50 to 85 per cent. W.

The *price of the ore* is calculated at £2 16*s*., for instance, for each per cent. of WO_3 per ton; thus, ore with 60 per cent. costs £168 per ton. In 1895 the price per cent. was 12*s*., in 1900 £1 10*s*., in 1904 £2 4*s*., in 1905 £1 5*s*., in 1907 £2 16*s*., in 1908 £1 5*s*., in 1909 £2 8*s*., and in 1911 £1 16*s*.

The price of *commercial metallic tungsten* (95 to 98 per cent.) also varies: 3*s*. 6*d*. per kilo in 1901, 5*s*. in 1903, 9*s*. 6*d*. in 1904, 5*s*. 2*d*. to 13*s*. 6*d*. in 1907, and 6*s*. in 1910.

DERIVATIVES OF TUNGSTEN. The valency of tungsten varies considerably in its various compounds, and thus chlorides containing 3, 4, 5, and 6 atoms of Cl are known. WCl_6, which is obtained from its elements on heating, forms a violet-black crystalline mass which is decomposed by water with formation of **Tungsten Trioxide, WO_3**. This compound is insoluble in water and acids, but dissolves in alkalis, forming the **Tungstates** from which acids separate **Tungstic Acid, $WO(OH)_4$**. This acid is capable of undergoing condensation with formation of various polyacids in a similar manner to chromium and molybdenum. With phosphates it forms compounds analogous to those which are obtained with molybdic acid.

According to Jannasch and Leiste (Ger. Pat. 266,973, 1910) tungstic acid may also be obtained by heating the ore, mixed with double or treble its weight of siliceous quartz, in a current of CCl_4 vapour. The iron chloride that distils is collected on dry potassium chloride, while CCl_4 also condenses (recoverable) and pure tungsten chloride; if the latter is condensed in dilute nitric acid, it forms pure tungstic acid. The various other metallic chlorides remain in the retort.

Tungstic acid is used for colouring porcelain.

TUNGSTEN DIOXIDE, WO_2, is highly suitable for making incandescent lamp filaments, and is obtained free from carbon and tungsten carbide by heating, electrically or in a furnace, tungstic acid to 800° in a graphite crucible surrounded by a clay crucible containing carbon; the CO formed reduces the WO_3 ($WO_3 + CO = WO_2 + CO_2$) and the resulting CO_2 is passed over red-hot coal to give CO again (U.S. Pat. 1,023,290, 1912). Farkas and Williams (U.S. Pat. 1,061,058, 1909 and 1913) first heat the tungstic acid in a tube in a current of CO_2 until it becomes black. A. Lederer (Ger. Pat. 199,107, 1906) heats the tungstic acid, mixed with glycerine or glycol, to bright redness for several hours in a covered crucible. *Sulphides, oxychlorides,* etc., of tungsten are also known.

SODIUM TUNGSTATE crystallises in bitter, nacreous, white scales, soluble in water to an alkaline solution, insoluble in alcohol and unalterable in the air. From its aqueous solution strong acids precipitate white tungstic acid, which becomes yellow in the hot and is soluble in ammonia. Stannous chloride gives, however, a yellow precipitate, which is turned blue in the hot by HCl owing to the formation of W_2O_5. Also with HCl and Zn, sodium tungstate solution gives an intense blue coloration.

These reactions serve to detect even traces of tungsten.

URANIUM TUNGSTATE and *calcium tungstate* are used for preparing the phosphorescent screens used in experiments with Röntgen rays.

URANIUM: U, 238.5

This is a heavy metal of a grey appearance similar to that of iron. It has a specific gravity of 18·7 and melts at above 1500°. It was formerly prepared by the electrolysis of the chloride and by heating this with sodium, but is to-day obtained together with uranium carbide, U_2C_3, by reducing the oxide with carbon in the electric furnace. It is found in combination in nature in the form of the oxide, U_3O_8, in **Uranite** and **Uraninite** (*pitch blende*), together with radio-active substances (p. 125), and abounds in Bohemia (Joachimsthal mines) together with Ni, Co, and Ag, and in North America, in compact or lamellar masses varying in colour from greyish-black to brownish-green and sometimes with yellow or green incrustations. This mineral (hardness 3 to 6 and density 5·9) is almost infusible in the blowpipe, insoluble in HCl and soluble in HNO_3; it contains 62 to 85 per cent. of the oxide mixed with 0·6 to 2 per cent. S, 4 to 7 per cent. Pb, about 4 per cent. Cu, 0·7 per cent. Zn, 0·5 per cent. Bi, 1 to 4 per cent. As and Sb, 2 to 13 per cent. SiO_2, 3 to 6 per cent. Fe_2O_3 and much radioactive matter.

The *United States* produced 24 tons of uranium oxide (corresponding with about 20 tons of the metal), almost all from *carnotite* (uranium vanadate) in Utah and Colorado, the crude mineral containing 0·5 to 6 per cent. of uranium oxide and 1·4 to 13·6 per cent. of vanadium oxide. *England* produced 95 tons of uranium ore in 1913 and 344 tons in 1914.

When uranium is finely subdivided it slowly decomposes water even at the ordinary temperature. It catches fire at 170°, and fixes nitrogen at 1000°, forming **Uranium Nitride.** Uranium compounds are as poisonous as those of arsenic.

URANOUS OXIDE : UO_2. This compound possesses basic characters and in it uranium is tetravalent. It is produced by reducing the trioxide with hydrogen.

Among uranous compounds the **Chloride, UCl_4,** the **Hydroxide, $U(OH)_4$,** etc., are known.

URANIC OXIDE : UO_3 (Uranium Trioxide). This compound has both basic and acid properties simultaneously. Theoretically it corresponds with the hydroxide, $U(OH)$, which is not known, but the **Metahydroxide, $UO_2(OH)_2$,** is known and has basic properties, being called **URANYL HYDROXIDE**; the divalent group UO_2, Uranyl, is found also in various other compounds. On heating the metahydroxide, UO_3 is obtained.

A well-known salt of this hydroxide is **Uranyl Nitrate, $UO_2(NO_3)_2 + 6H_2O$,** which forms greenish-yellow crystals yielding UO_3 at 250°. When uranium nitrate crystals are treated with acetic anhydride and a little glacial acetic acid, violent evolution of NO_2 occurs, while uranyl acetate, $UO_2(CH_3CO)_2$, remains (L. Vanino, 1911). Another salt is **Uranyl Sulphate, $UO_2SO_4 + 6H_2O$,** which forms needle-shaped yellow crystals.

On treating the solution of a uranyl salt with sodium hydroxide, a yellow precipitate of sodium uranate, $U_2O_7Na_2$, is formed which is soluble in acids. It is used technically for the production of a yellow fluorescence in glass.

On heating uranic or uranous oxide, the oxide U_3O_8 is obtained, which is found in nature as **Uranite,** and may be considered as the **Uranate of Uranous Oxide, $UO_2,2UO_3$.**

SEVENTH GROUP

MANGANESE: Mn, 55

Whilst in the case of chromium derivatives we find a certain analogy with those of sulphur, in manganese compounds we notice constitutional analogies with certain chlorine derivatives. Thus potassium permanganate, $KMnO_4$, is isomorphous with potassium perchlorate, $KClO_4$, and chlorine heptoxide, Cl_2O_7, has its counterpart in manganese heptoxide, Mn_2O_7. In both cases the manganese is heptavalent. In its more or less red-coloured derivatives, manganese exerts varying valency, being di-, tri-, tetra-, hexa-, or heptavalent, and thus we have manganous compounds, manganic compounds, and salts of manganic and permanganic acids. These compounds show a certain analogy with those of chromium and iron.

Manganese is not found free in nature, but is widely diffused in abundance in its minerals,[1] in agricultural soil, and in small quantities (but with important catalytic effect) in the blood, in excreta, plants, urine, many meteorites, mineral waters, etc.

The metal, which is a grey lustrous substance, is now obtained pure by the Goldschmidt process (p. 727) from a mixture of manganese oxide with powdered Al. It was formerly obtained in a less pure condition from manganese chloride with sodium or from the oxide and carbon in the electric furnace. Whilst it cost £26 per kilo in 1885, it cost only 16*s*. in 1910, whilst the industrial product free from Fe and C costs 6*s*. 5*d*. It is very hard, has a specific gravity

---

[1] *Braunite*, Mn_2O_3 (shining blackish-brown, density about 4·8, hardness 6, infusible); *Hausmannite*, Mn_3O_4 (mangano-manganic oxide), forms shining, grey tetragonal pyramids, density 4·7, hardness 5; *rhodocrosite* (*spathic manganese ore*), $MnCO_3$, with considerable impurities of Fe, Mg, Ca, etc.; *Franklinite*, a mixed oxide of Mn, Fe and Zn; *Knebelite*, silicate of Mn and Fe; *Hauerite* or *manganous pyrites*, manganous sulphide; *Rabdionite*, mixture of oxides of Mn, Cu, Co. The most abundant and most important manganese mineral is, however, *Pyrolusite* or manganese dioxide, MnO_2, which forms compact, often fractured, shining masses with a radiating crystalline structure and of blackish brown-grey colour; the powder is black. Its density is about 5 and its hardness about 2. At a red heat it yields oxygen, whilst with HCl it gives Cl. It contains 30 to 90 per cent. of MnO_2 according to the purity (as impurities it contains up to 30 per cent. Fe_2O_3, 3 per cent. Al_2O_3, 4 per cent. CaO, 20 per cent. SiO_2, 1 per cent. P_2O_5, etc.). The commercial value of pyrolusite depends on the richness in MnO_2 (*see* p. 154), but for the metallurgical industry preference is given to ore containing less than 0·1 per cent. P_2O_5 (Brazil, Chili, Cuba, Japan, France, Turkey); that from India, the Caucasus and Greece contains up to 0·3 per cent. P_2O_5. Less important manganese ores are *manganite*, hydrated manganic oxide (dark iron-grey, trimetric, radiating crystals, density 4·3, hardness 2·5 to 4·5); *varvicite*, hydrated oxide and peroxide of manganese; *psilomelan*, which contains mixed oxide, *i.e.*, manganous oxide and peroxide in brown or bluish-black crystalline masses of density 4·1 and hardness 6.

Manganese minerals are found in France (Saône et Loire, Ariège), Spain (Huelva, Alexia, Cavadonga), Germany (Ilfeld, Thuringia, Hesse, Harz, Nassau), Russia (abundant in Caucasus, Baku, Tiflis), Bosnia, Bukovina, Macedonia, Greece, India (abundant at Madras, Bombay, Sandur, Mysore), Japan, United States (Arkansas, Virginia, Georgia), Canada, Columbia, Cuba in Chili (Atakama and Coquimbo), Brazil (Bahia, Minas Geraes), etc.

In *Italy* prior to 1914 manganese ores for glass-making and later for the metallurgical industry, were furnished by the mining district of Carrara, including Liguria (Nè, Maissana, Casarza, Framura, Bonassola, Pignone) and by Sardinia (Carloforte), the mean content of Mn being 44 per cent. Since 1914, however, large amounts of ore have been obtained in the mining districts of Florence (Leghorn, Pisa, Siena and especially Rio Marina), with an average of 22 per cent. of Mn. The content may be increased by screening the ore, as was commenced in Sardinia, where the deposits are covered with diaspore and with red, yellow and violet ochre; less important deposits occur in Piedmont (Coria Canavese, St. Marcel).

of 7·8 to 8, and melts at 1260°. It oxidises readily in the air and dissolves even in dilute weak acids to form manganous salts. In the form of a fine powder it decomposes boiling water. It is much used in metallurgy to prepare manganiferous cast- and wrought-iron and also certain bronzes; as borate or resinate of manganese it is employed as a dryer for linseed oil (*see* Vol. II., "Organic Chemistry").

STATISTICS. The production of *manganese ore* in different countries is as follows: *British India:* 3000 tons in 1893, 175,000 in 1903, 917,440 in 1907, 685,104 in 1908, 813,760 in 1910, 637,444 in 1912, and 850,000 in 1913. *Brazil:* 236,778 tons in 1907, 254,000 in 1910, 155,000 in 1912. *Australia:* 2500 tons in 1907. *Cuba:* 14,000 tons in 1906. *Japan:* £4000 in 1904, £52,000 in 1906, 10,410 tons (about 80 per cent. MnO_2) in 1907, 11,120 in 1910, 8362 in 1912. *Greece:* 10,000 tons in 1907, 733 in 1911. *Sweden:* 4300 tons in 1907, 5750 in 1910, 5100 in 1912. *Belgium:* 2100 tons. *England:* 16,356 tons in 1907, 5554 in 1910, 5394 in 1913, 3437 in 1914; imports: 330,000 tons in 1909, 482,000 (£960,000) in 1910. *Germany:* 51,463 tons in 1905, 68,000 in 1908, 80,600 in 1910, 92,500 in 1912; imports: 263,000 tons in 1905, 200,000 in 1909. *Austria-Hungary* (and Bosnia): 26,000 tons in 1907, 33,000 in 1910, 17,500 in 1912 and 20,500 in 1913. *Russia:* 928,000 tons (especially in the Caucasus: 87 to 88 per cent. MnO_2) in 1907, almost all exported; in 1910 the Caucasus produced 580,000 tons and the Urals (at Nikopolrayon) 190,000 tons; the Russian output was 766,000 tons in 1912 and 1,310,000 in 1913. *United States:* 6446 tons of good ore in 1908, 784,464 (including manganiferous iron ore) in 1910, 990,000 in 1912 and 791,500 in 1913; imports: 242,000 tons in 1910, 177,000 (£240,000) in 1911, 585,570 in 1916, and 729,596 in 1917; also much ferro-manganiferous ore (1,243,400 tons in 1907 and 539,000 in 1908) and zinco-manganiferous ore (112,000 tons in 1908). *Cuba:* 30,500 tons in 1907. *Spain:* 41,500 tons in 1907, 8600 in 1910, 20,000 in 1912, and 22,350 in 1913. *France* exported 1705 tons in 1913, 411 in 1914, and 40 in 1915; the imports were 259,000 tons (£920,000) in 1913 (one-half from Russia), 153,487 in 1914, and 12,590 in 1915. In 1907 France produced 18,000 tons of manganese ore, 7925 in 1910, 5576 (of moderate quality) (£6920) in 1912.

The statistics for *Italy* are (tons):

	1906	1909	1911	1912	1913	1914	1915	1916	1917
Production	3,050	2,750 (£3,640)	3,515	2,641	1,622	1,649	12,577	18,174 (£25,000)	—
Importation	—	—	—	—	—	13,943	15,972	29,925	21,538

Commercial fused metallic manganese cost before the European War about £200 per ton and the chemically pure metal 16*s*. per kilo.

The price of manganese ore of high quality (above 80 to 85 per cent.) before the European War was about £4 per ton. During the war the price in Italy and France exceeded £40 in 1917 and £60 in 1918 (mostly for Japanese ore).

MANGANOUS OXIDE: MnO. This is obtained as a green powder by reducing the other oxides in hydrogen or by heating the carbonate in the air, but when heated for a long time it is transformed into Mn_3O_4.

MANGANOUS HYDROXIDE: $Mn(OH)_2$. If an alkali hydroxide is added to a solution of a manganous salt free from air, this compound separates as a white mass which readily oxidises in the air and then becomes brown.

The hydroxide is not obtained with NH_3 if NH_4Cl is present in solution, because a complex ion is formed, as in the case of magnesium (pp. 101, 671).

MANGANOUS CHLORIDE: $MnCl_2$. This is formed in large quantities in the manufacture of chlorine (p. 153), and may be obtained in pink hygroscopic crystals containing 4 mols. of water of crystallisation. It is sometimes used in dyeing (at £14 per ton), and is re-utilised in the manufacture of chlorine.

MANGANOUS SULPHATE: $MnSO_4$. This compound is obtained by dissolving the carbonate in sulphuric acid or by heating manganese dioxide to redness with ferrous sulphate and then extracting with water. It crystallises with 4 to 7 mols. of water and has a fine pink colour; the crystals containing $7H_2O$ are isomorphous with ferrous sulphate. On heating, the last molecule of water is eliminated only at 280°. With alkali sulphates it forms double salts which crystallise with $6H_2O$, and are isomorphous with magnesium sulphate. It is used in dyeing and in painting porcelain. The anhydrous salt costs £18 to £22 per ton.

MANGANOUS SULPHIDE : MnS. This compound is of a pale flesh colour, in which respect it differs from the other sulphides, and since it is soluble in acids it is obtained from manganous salts with alkali sulphides, but not with H_2S.

MANGANOUS CARBONATE : $MnCO_3$. This compound is found in nature as *Rhodochrosite,* $MnCO_3$, and is formed by the action of alkali carbonates on manganous salts. It first separates as a white mass which is oxidised by the air and then becomes brown.

MANGANIC OXIDE : Mn_2O_3 (Sesquioxide). This compound is obtained on heating the other oxides of manganese in a current of oxygen. It is found in nature as *Braunite;* with H_2SO_4 it forms manganous sulphate and separates MnO_2.

MANGANIC HYDROXIDE : $Mn(OH)_3$. This separates as a brown substance on leaving an ammoniacal solution of a manganous salt exposed to the air. It has very weakly basic properties and its salts are consequently hydrolytically decomposed by water. It is soluble in HCl, with which it forms a brown liquid which evolves Cl on heating, and is perhaps transformed into $MnCl_4$.

The **METAHYDROXIDE : $MnO \cdot OH$, $H_2Mn_2O_4$, or Mn_2O_3,H_2O,** is found in nature as *Manganite,* which forms black crystals.

MANGANO-MANGANIC OXIDE : Mn_3O_4 (Mixed Oxide). This oxide is the most stable and is formed when the other oxides are heated for a prolonged period in the air. It is found naturally as *Hausmannite,* Mn_3O_4, and consists of a reddish-brown powder which liberates chlorine on heating with HCl.

MANGANIC SULPHATE : $Mn_2(SO_4)_3$. This compound is obtained on dissolving manganic oxide in H_2SO_4, or a mixture of manganous and manganic sulphates is obtained by treating the mixed oxide, Mn_3O_4, with concentrated H_2SO_4. It dissolves in water with a deep red colour.

MANGANIC PERSULPHATE : $Mn(SO_4)_2$, is prepared by the electrolytic oxidation of manganous sulphate and forms a black substance which can be obtained in solution only in presence of sulphuric acid. It has extraordinary oxidising properties and is used for this purpose in the manufacture of organic products (Fr. Pat. 338,990 of 1903).

MANGANESE DIOXIDE : MnO_2. This is found in nature as a dark mass in the form of *Pyrolusite,* which is the most abundant manganese ore, and is used in the manufacture of chlorine. On heating to dark redness it forms $Mn_2O_3 + O$, and at a bright red heat $Mn_3O_4 + O$. It dissolves in cold HCl without evolution of chlorine, but at high temperatures the dark yellow solution of $MnCl_4$ thus formed decomposes into Cl_2 and $MnCl_2$. In the section on chlorine (pp. 154 *et seq.*) we have described the various processes for regenerating manganese dioxide from various salts, especially from the chloride. We have also explained the tests used in determining the value of manganese dioxide.

The dioxide is readily dissolved by a solution of SO_2 or sodium bisulphite and this reaction is utilised for dissolving the dioxide deposited on fabrics bleached with potassium permanganate.

Manganese dioxide was formerly largely used in the manufacture of Chlorine (*see* p. 153). When it contains little or no iron it is used in glass-making (*see* p. 634) and when of high quality (85 to 90 per cent. MnO_2) it serves for making dry electric batteries; much is also used for making manganiferous cast- and wrought-iron. Besides the natural dioxide (pyrolusite) there is also on the market artificial manganese dioxide, recovered from chlorine works; this is obtained by precipitating the hydroxide from a soluble manganese salt by alkali and oxidising the manganous hydroxide in the air by means of hypochlorite. It then forms a dark-brown powder or paste, which dissolves in hydrochloric acid but withstands the action of light and many chemical reagents. It readily forms a paste with gum and is then used as a water colour and in dyeing cotton *khaki* (the cotton is steeped in manganous chloride or sulphate, treated with alkali and oxidised with calcium hypochlorite).

The *price* in ordinary times was £3 4*s.* per ton for 60 per cent. quality, £3 12*s.* for 70 to 75 per cent., and £6 8*s.* for the highest quality; the powder costs 15 per cent. more. During the European War the price in Italy rose to £100 per ton. Its use as a *catalytic fertiliser* (*see* p. 350) seems now abandoned.

The hydroxides $MnO(OH)_2$ and $Mn(OH)_4$ correspond with the dioxide, and are obtained by adding a hypochlorite or a permanganate to a solution of a manganous salt.

COMPOUNDS OF MANGANIC AND MANGANOUS ACIDS

The manganates correspond with the formula, $MnO_4X'_2$, and the permanganates with MnO_4X'. When any compound of manganese is fused at a dark-red heat with potassium hydroxide or carbonate in presence of an oxidising agent such as KNO_3 or $KClO_3$, a green mass results which is soluble in water (non-alkali manganates are insoluble) and which, after concentration *in vacuo*, separates rhombic prisms of **Potassium Manganate, K_2MnO_4,** which are isomorphous with the chromate and with K_2SO_4.

If MnO_2 is heated with KOH without an oxidising agent, only one-third of the manganese is transformed into manganate: $3MnO_2 + 2KOH = Mn_2O_3 + K_2MnO_4 + H_2O$, whilst with an oxidiser the utilisation of the manganese is much improved and theoretically should be complete according to the equation: $MnO_2 + 2KOH + O = K_2MnO_4 + H_2O$, without formation of sesquioxide.

When boiled with much water, it is decomposed with separation of part of the MnO_2, the solution becoming violet through the formation of potassium permanganate:

$$3K_2MnO_4 + 2H_2O = MnO_2 + 4KOH + 2KMnO_4.$$

Thus a green solution has become violet (hence the name of *mineral chameleon*), whilst it is not altered by alkalis.

The transformation of green manganate into violet permanganate is still more rapid under the action of acids (even weak acids like CO_2), chlorine, or ozone:

$$K_2MnO_4 + Cl = KMnO_4 + KCl \quad \text{or}$$

$$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O.$$

Oxidation with chlorine gives complete conversion into permanganate, the same result being reached by electrolysing *pure* manganate solutions (the manganate obtained by fusion with alkali chlorate or nitrate cannot be used, excess of these salts being deleterious to the electrolysis): $2K_2MnO_4 + H_2O + O = 2KOH + 2KMnO_4$; the caustic potash is recoverable.

On treating violet solutions of permanganates with hot concentrated alkalis green manganate solutions are regenerated.

POTASSIUM PERMANGANATE: $KMnO_4$. This is prepared industrially by the Woehler process by mixing 500 kilos of a solution of KOH of sp. gr. 1·44 with 105 kilos of $KClO_3$ and adding finely powdered MnO_2; the whole is boiled, evaporated, and the residue fused in crucibles at a dull red heat until it has acquired a pasty consistency and the decomposition of the chlorate is complete. The potassium manganate, K_2MnO_4, thus obtained is dissolved by boiling with much water, whilst a current of chlorine, CO_2, or ozone is passed into the liquid. The permanganate separates in the crystalline form from concentrated solutions, even in presence of KOH which is formed during the reaction (*see above*) and is separated from the dissolved substances in a hydro-extractor. Without chlorine 100 kilos of MnO_2 yield 100 kilos of permanganate, but with chlorine the yield is sensibly increased. Potassium nitrate is sometimes used instead of the chlorate in the fusion; Béchamp melts 10 parts of finely powdered MnO_2 and 12 parts of caustic soda fused with a little water, the mass being brought to dryness, spread out on suitable trays, oxidised with oxygen until saturated, allowed to cool, extracted with boiling water, and the manganate converted into permanganate by means of a current of CO_2; after twenty-four hours the liquid is decanted off and allowed to crystallise: 1 kilo of MnO_2 yields 350 grams of permanganate in the first crystallisation. O. Dieffenbach (Ger. Pat. 195,523) prepares it by electrolysing KOH solution of 35° Bé. in which powdered MnO_2 and a little permanganate are suspended. Messrs. E. Schering obtain permanganate by the electrolytic oxidation of manganate; it appears that 0·7 kilowatt-hours are consumed per kilo of permanganate and that two-thirds of the manganate are converted into permanganate, no diaphragms being used. The total consumption of coal is 25 kilos per kilo of pure permanganate manufactured.

Messrs. Meister, Lucius and Brüning of Höchst prepare permanganate as follows: powdered MnO_2, in a large, flat-bottomed, cast-iron pan with a stirrer, is heated carefully over direct fire with caustic potash of 50° Bé. (95 kilos of 50 per cent. MnO_2 and 95 litres of caustic potash solution containing 65 kilos KOH) until the whole mass becomes dry, stirring being interrupted occasionally to powder the mass, which tends to form lumps, these having to be broken with a hammer to allow the stirrer to work.

In twelve hours the transformation reaches its maximum, 65 per cent. of the MnO_2 being changed into manganate if good ore is used, or only 45 per cent. with recovered ore. In this fusion 100 kilos of coal are used per 100 kilos of ore. The solid, lumpy mass is powdered rapidly in mills (otherwise it absorbs moisture and becomes difficult to powder). Oxidation is carried out in another double-bottomed pan furnished with a stirrer and heated over direct fire (lead being poured into the jacket); it is well closed except for an exit for the superheated compressed air injected into the pan for twelve hours while the pulverulent mass (about 300 kilos) is kept at 260° to 270°; if the mass is too dry, the air carries away much dust, and it should be wetted slightly with KOH solution. The greenish mass becomes blue at the end and is carried to a mixer to be extracted with alkaline mother-liquors (electrolytic, washing and crystallising liquors from permanganate) showing about 25° Bé. at 40°. After standing, the solution is decanted off and the insoluble MnO_2 paste collected in filters and washed, the wash liquors being added to the original filtrate, which should show 40° Bé. The liquid is then electrolysed at 30° with 30 to 40 amps. per sq. dm. (2·5 to 2·7 volts) for twelve hours with anodes consisting of nickel plates arranged in a hexagonal ring and cathodes of six iron plates, which form a revolving ring concentric with the anode; the bath is of sheet iron. The permanganate solution, mixed with crystals already separated, is discharged into a cooling cylinder with stirrer, and when crystallisation is complete the crystals are separated by centrifugation, washed with cold water and dried in a vacuum; their purity in then 99 per cent. (*see also* Ger. Pat. 118,232 and 195,523). Potassium permanganate forms rhombic crystals, isomorphous with $KClO_4$, of a blackish appearance but with a green metallic reflex.

100 grams of water dissolve:

at . .	4°	10°	20°	30°	40°	60°	70°	75°
grams $KMnO_4$	3·36	4·40	6·51	9·06	12·53	22	28·6	32·35

Permanganate dissolves also in glacial acetic acid, pyridine, acetone, methyl alcohol, liquid ammonia, etc. The aqueous solution has an intense violet-red colour and exhibits a strong oxidising action on organic and inorganic compounds. Sodium permanganate is far more soluble than the potassium salt and deliquesces in the air. Calcium permanganate is also highly soluble, and is obtained by electrolysis of $KMnO_4$ in presence of calcium salts, KOH being recovered (Ger. Pat. 145,368, 1901).

The solutions of various permanganates all show the same spectrum, which indicates that they all have the same MnO'_4 ion in common.

In acid solution every 2 mols. of permanganate liberate 5 atoms of oxygen: $2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$; the end of the oxidation of a substance by permanganate is recognised by the permanence of the violet coloration due to the latter, so that no indicators are used, as the colour of manganese sulphate is not perceptible in dilute solution.

In neutral or alkaline solution, only 3 atoms of oxygen are evolved:

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O.$$

The oxidation of a ferrous salt by permanganate in acid solution proceeds thus: $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$.

When heated at 240°, permanganate decomposes with evolution of oxygen: $2KMnO_4 = MnO_2 + K_2MnO_4 + O_2$. Permanganate solution is not altered by pure alkali, but in presence of organic compounds, *e. g.*, alcohol, these undergo oxidation, the solution becoming first green (formation of manganate) and then colourless. Treatment of powdered permanganate with concentrated H_2SO_4 gives ozonised oxygen and red vapours of permanganic acid; with dilute H_2SO_4 oxygen is evolved, and on gentle heating colourless manganous sulphate remains. Permanganate is instantly reduced by reducing agents (these being oxidised), *e. g.*, H_2S, PH_3, HI, SO_2, H_3PO_3, H_3AsO_3, ferrous salts, etc.; it oxidises ammonia to nitrous acid in the cold and to nitric acid in the hot. Organic compounds are oxidised more or less rapidly (as far as CO_2, as easily happens with acetic and formic acids, etc.) according to the temperature and the reaction of the medium.

With feebly acid aqueous solutions, reducing substances give Mn_2O_3 directly, but with alkaline solutions the green manganate is formed first, this then giving Mn_2O_3.

Permanganate is used for the preservation of timber and for bleaching textile fibres by immersing them for some time in an aqueous solution of $KMnO_4$ and then dissolving the MnO_2 with sodium bisulphite. It is used as an oxidising agent in the manufacture of many organic compounds (*e. g.*, "saccharin," dyestuffs, drugs, etc.), and it is also used for purifying various gases, such as CO_2, H, NH_3, etc., and is an energetic disinfecting and oxidising agent. Thus it transforms ferrous salts into ferric salts, nitrous acid into nitric acid, and oxalic acid into CO_2, and reacts with H_2O_2 with liberation of oxygen. Crude potassium permanganate cost before the war £15 4*s.* per ton, and when crystalline £40 per ton; it was made mostly in Germany and to some extent in Austria. During the European War the price of pure permanganate in Italy, France, England and America—required especially in making saccharin—rose to £1 12*s.* per kilo in 1917 and in Italy to £3 12*s.* per kilo in 1918.

France in 1913 imported 270 tons of permanganate, the production being zero. Italy in 1910 imported 15 tons (£600) of potassium permanganate, 43 tons in 1913, 62 in 1914, 57 in 1915, and 5 in 1916.

PERMANGANIC ANHYDRIDE : Mn_2O_7 (Manganese Heptoxide). This compound is obtained as a dark oil on adding very cold concentrated H_2SO_4 to dry $KMnO_4$. It is a powerful oxidising agent which sets fire to paper, alcohol, etc. (*Translator's note.*—This compound is extremely explosive.)

EIGHTH GROUP

This is the last group of the periodic system, and may be divided into three sub-groups :

(*a*) Iron, Fe, 55·85; Nickel, Ni, 58·67; Cobalt, Co, 58·95.
(*b*) Ruthenium, Ru, 101·7; Rhodium, Rh, 102·9; Palladium, Pd, 106·7.
(*c*) Osmium, Os, 190·9; Iridium, Ir, 193·1; Platinum, Pt, 195.

(a) IRON GROUP

Iron, nickel, and cobalt are distinguished from the other metals by their very pronounced magnetic properties, being attracted by a magnet. Those iron compounds in which the iron is most highly oxidised (*ferric* compounds) are the most stable, whilst in the case of nickel and cobalt the less highly oxidised compounds are the more stable, as in the case of copper and zinc.

IRON: Fe, 55.85

This important metal is found native only in rare instances and in small quantities, whilst it abounds in the native state in stars (the sun, etc.), where a high temperature exists in presence of an atmosphere of glowing hydrogen. It is sometimes found on the earth in the form of *meteorites* (*meteoric iron*), which occur in blocks up to a weight of 8 or even 15 tons. This iron is not usually homogeneous, but is capable of being worked, does not contain chemically combined carbon, but almost always contains 4 to 10 per cent. of nickel. In Fig. 316 we show a *micrograph* of meteoric iron obtained by Widmanstätten by the method already described on p. 515. In this figure we see regular designs due to crystals of compounds of iron with nickel and with phosphorus.

On the other hand, iron ores are extremely abundant in the earth's crust, and consist of the oxides *Magnetite* or *Magnetic Iron Ore*, Fe_3O_4, *Hœmatite*, Fe_2O_3, *Specular Iron Ore* (anhydrous crystalline, Fe_2O_3), and also as *Limonite*, $Fe_2O_3,2H_2O$ and $2Fe_2O_3,H_2O$, *Spathic Iron Ore* or *Siderite*, $FeCO_3$, and *Iron*

Pyrites, FeS_2, in which ore the sulphur is first utilised. Some iron ores contain much manganese and others are rich in titanium. Iron ores are especially abundant in England, the United States, Germany, Luxemburg, Russia, France, Spain, Sweden, Austria, China, etc. In Italy there is not much iron ore, but the most important deposits are those on the island of Elba, where specular iron ore is abundant, and in Sardinia, where there is hæmatite, and a little spathic iron ore in the Val Trompia and Val Camonica in Lombardy; in the Val d'Aosta there are deposits of magnetite and specular iron ore.

PROPERTIES OF IRON. Iron may be obtained chemically pure by reducing pure iron oxide by heating it in a current of hydrogen, or preferably by precipitating Mohr's salt (ferrous ammonium sulphate) with potassium oxalate and igniting the iron oxalate after washing it. The product is then washed with acid and reduced by heating in a current of pure hydrogen. Very pure iron is also obtained electrolytically. Chemically pure iron has a silvery appearance and a specific gravity of 7·84, and is insoluble in HCl; it melts at about 1530° and expands on solidification.

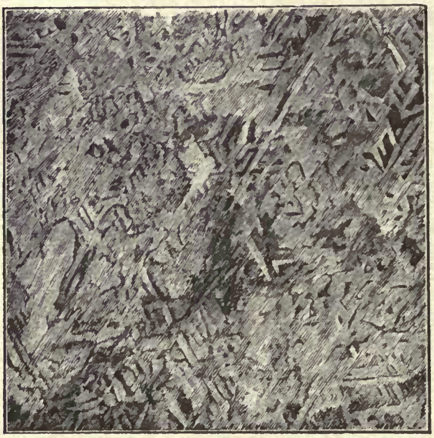


FIG. 316.

Pure iron is of no particular importance, but becomes valuable when small quantities of other elements are present, such as C, Si, Mn, etc. Wrought- and cast-iron can only be temporarily magnetised, whilst steel can be magnetised in a permanent manner. The metal is not attacked by water free from CO_2, or even by dry air, and still less by alkaline water, whilst, on the other hand, it rusts easily in moist air, with formation of ferric hydroxide.

Of the various theoretical explanations of the formation of *rust*, the two following seem the most acceptable: According to the first, iron immersed in pure water would not rust even in presence of oxygen, but this is brought about by a minimal trace of an acid, even carbonic, which acts as a catalyst. Thus it gives first ferrous bicarbonate: $Fe + O + H_2O + CO_2 = FeH_2(CO_3)_2$, which decomposes as follows: $2FeH_2(CO_3)_2 + H_2O + O = 2Fe(OH)_3 + 4CO_2$. The CO_2 liberated then acts again as before, a very small amount of carbonic acid thus producing extensive rusting. According to the electrolytic theory, on the other hand, iron immersed in water (which may be regarded as ionised to a very small extent) loses positive iron ions, which pass into solution in the water, while at the same time hydrogen ions leave the water, and there remains in solution ferrous hydroxide, which gives ferric hydroxide with atmospheric oxygen.[1]

According to J. N. Friend (1909) pure iron combines with the oxygen of the air (even dry) the more rapidly the higher the temperature, and in contact with water vapour iron only loses its lustre at 350°, whereas at 775° the steam is considerably dissociated.

When heated in the air iron becomes covered with a scaly layer of Fe_3O_4. It decomposes steam at a red heat with formation of ferroso-ferric oxide, Fe_3O_4, and hydrogen, but the reaction is reversible as this oxide is reduced by hydrogen

---

[1] *Preservation of iron from rusting.* Of the various processes suggested, many of which are in common use (coating of the iron with minium or paint, smearing with vaseline or mineral oil, burnishing, etc.), mention may be made of the following: The iron or steel articles are heated in a concentrated boiling solution of iron phosphate and a little free phosphoric acid, or, according to Ger. Pat. 272,451 of 1913, iron objects may be smeared with thorium nitrate solution (or salts of Al, Mg, Zr, Cr) mixed with a little dextrin, allowed to dry and then heated to redness.

The ease with which *steel* corrodes increases as the proportion of carbon increases and as the proportions of P and Mn diminish, but the physical structure (fibrous, etc.) is of greater influence.

on heating: $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$. Iron dissolves in HCl and in H_2SO_4 with evolution of hydrogen, whilst when dissolved in dilute HNO_3, NO is evolved; in concentrated nitric acid it becomes passive. It becomes passive also in an atmosphere of CO, but not of hydrogen, so that passivity apparently depends on a layer of oxygen and not of hydrogen (*see* pp. 512, 794). Red-hot iron burns in oxygen with production of sparks and of very intense light.

A quality of iron called *neutral iron* is to-day obtained which resists the action of sulphuric and nitric acids at various concentrations, both hot and cold. Its resistance exceeds that of the most highly carbonised iron. The process of manufacture is kept secret.

METALLURGY OF IRON. This is based on the reducing action of carbon at high temperatures by which comparatively infusible iron is liberated from the oxides; this then dissolves carbon at high temperatures, becoming readily liquefied and forming cast-iron, whilst the greater portion of the carbon is evolved in the form of CO and CO_2, thus:

$$Fe_2O_3 + 2C = 2Fe + CO + CO_2.$$

The impurities are eliminated during smelting by the use of fluxes which form an easily fusible, separable slag.[1]

According to the nature of the ore, but more especially according to the carbon contained in the product and the method by which it is worked, the following varieties of commercial iron may be distinguished, as defined by an International Commission at Philadelphia in 1876.

IRON	CAST-IRON OR PIG IRON containing 2·3 to 5 per cent. of C, non-malleable, readily fusible and non-weldable.	Common *grey cast-iron* containing a large portion of its carbon in the uncombined (graphitic) state and a smaller portion in combination.	
		White cast-iron containing 3 to 5 per cent. of carbon combined as the iron carbides, FeC_4, FeC_3, Fe_3C_2, and 0·2 to 0·5 per cent. of graphitic C.	
	MALLEABLE IRON containing 0·02 to 2·3 per cent. C, and fusible with difficulty.	Fused iron containing 0·05 to 2·3 per cent. of C.	If tempered it is *cast steel* (Bessemer and open-hearth steel), containing 0·5 to 2·3 per cent. of C.
			If non-tempered it is *soft steel* (Bessemer and open-hearth), containing 0·05 to 0·55 per cent. of C.
		Unfused iron—softened or welded—containing 0·02 to 0·5 per cent. of C.	If tempered, *cementation steel* or *puddled steel,* containing 0·2 to 0·5 per cent. of C.
			If non-tempered, *wrought-iron,* worked or puddled, containing 0·02 to 0·2 per cent. of C, which is almost entirely combined.

---

[1] Iron was not the first metal to be prepared and worked by man, as it was not commonly found native, but it followed immediately on copper. It is not clear how it was extracted by primitive peoples. It is certain that they treated iron ores in a very rudimentary and imperfect manner, and the resulting metal was certainly not very good. They also first treated meteoric iron, and iron objects are known which were made by the ancient Egyptians at least 5000 years B.C., and by the Chinese about 3000 B.C.

Something very analogous to the primitive smelting of iron is still met with on the western coasts of India and amongst certain African tribes. The oxide is reduced with wood charcoal in a kind of cylindrical clay furnace about 1 metre high and 30 cm. wide, or in a kind of hearth excavated in the ground. Air is injected by bellows formed of goat skins and bamboo tubes, but a homogeneous fused mass cannot be obtained. For many centuries the iron produced at Damascus and Toledo was celebrated, because in these places they understood how to prepare the most varied objects from spongy iron by working it with the hammer.

In the Middle Ages the iron industry developed throughout the world, but the process of working was always primitive and the iron was reduced with wood charcoal.

Nowadays, however, the percentage of carbon no longer suffices to distinguish steel from cast-iron, other physico-chemical criteria, illustrated later, being employed.

The ores which are used for the preparation of iron, which contain 30 to 60 per cent. of Fe, are sometimes roasted in heaps or in cupola furnaces in order to remove water, CO_2, As, S, etc., and to break down the compact lumps and oxidise ferrous oxide, which is reduced by carbon with more difficulty than ferric oxide. Poor and rich ores are then *blended* according to the local conditions in order to obtain the maximum yield of iron, and the *flux* is added in such a way that the mixture does not contain more than 50 per cent. of iron. The purpose of the flux is to remove the impurities, S, P, Ca, etc., and then to facilitate the fusion of the iron into a homogeneous mass. If the ore contains a gangue rich in calcium and magnesium, quartz and substances containing much silica and alumina are added, whilst if the gangue of the ore contains much silica or alumina, limestone or dolomite is added in order always to obtain, at temperatures close to the melting-point of the iron, a slag of molten silicates which removes all impurities from the molten iron and carries them to the surface, thus also preserving the molten iron from oxidation by the air blown into the blast furnace.

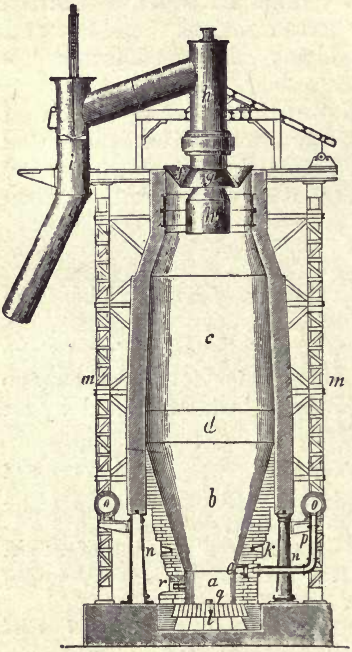


FIG. 317.

The ore is mixed with the flux, and its reduction to free iron is conducted in large cupola furnaces, called *blast furnaces* (Fig. 317), which are about 20 to 30 metres high and have a diameter of 5 to 7 metres. The largest of these furnaces, which are erected in America and are up to 37 metres high, cost £80,000 to £120,000. The mixture of ore and flux is introduced through the upper mouth by pouring it into *f*, and then raising the pipe, *g*, with a lever, so forming a slit through which the mixture falls into the furnace. This mixture is introduced alternately with charges of metallurgical coke (or wood charcoal, or sometimes even anthracite). At one time these furnaces were constructed of brickwork of great thickness and with a wide base, entirely of refractory materials. The internal shape was that of two truncated cones, united by a wider base. To-day they are somewhat simplified, as they are built with comparatively thin fireclay walls tightly held together and enclosed by iron plates.[1] The shape of the furnace is generally that indicated in the Figure.

---

[1] A true revolution in the smelting of iron was started at the beginning of the thirteenth century by a modification of the system of heating the ore. In Franconia and in Siegerland (Prussia) the first *blast furnaces* were then erected, in which the heat was better utilised by surrounding the whole mass of ore and fuel by a form of brickwork cupola, and driving the blowers which injected air by means of water wheels. We then see the smelting of iron migrate from the top of the mountains towards the valleys in order to utilise water-power, but these blast furnaces led from the commencement to many surprises which seriously embarrassed the metallurgists of that time. The higher temperature and the absorption of carbon by the iron no longer led to a pasty and spongy product which was easily worked with a hammer, but to a product which was liquid at a red heat and which could no longer be wrought after solidification, as it was very brittle and could not be welded. *Cast-iron* was thus produced, involuntarily, for the first time. It was, however, soon found that after further treatment the cast-iron again became malleable and similar to the iron which had been prepared in the past, but of better quality. In 1500 the new process was carried out in blast furnaces which reached a height of 4 to 5 metres, and in addition to work in wrought-iron, cast-iron articles of the most varied kinds were also produced, and were used for artistic and industrial purposes.

Germany with its great forest wealth maintained itself at the head of Europe during several centuries in iron production, but no important innovations were introduced into this industry until the eighteenth century. Attempts were made in England in 1729, and before that in Belgium in 1627, to replace wood charcoal by coal and to smelt the ore in reverberatory furnaces with coke specially prepared in a species of oven, but did not lead to practical results. Nevertheless in 1619 Dud Dudley worked for several years with coal, and was able to sell the iron produced at £4 per ton, whilst that prepared with wood charcoal cost £6 to £6 8*s*.

In the space above *c* (the *stack*) *drying* occurs at a temperature of about 400°; the *reduction* of the ore occurs at a temperature of 1000° to 2000° below and 400° above. At the widest point, *d*, called the *belly* of the furnace, the iron commences to soften and to absorb carbon. *Carburisation* occurs in the conical part, *b*, called the *boshes*, where the temperature rises from 1200° to 1600°, and the iron absorbs carbon and gradually becomes more fusible, finally collecting as a liquid covered with molten slag in the cylindrical zone, *a*, called the *hearth*. Below *a* the fusion of the iron is complete, as the temperature rises to 1800°, and at that point a strong blast of air passes into the furnace from several tuyères, *e*, at a height of a metre and a half above the floor, causing the combustion of the carbon, so that the temperature in this zone rises to 2600°. The lower part of the hearth forms the *crucible* in which the liquid cast-iron collects, covered by molten slag, which protects it from oxidation. The slag is discharged by the mouth, *r*, whilst the cast-iron is discharged through the opening, *g*. The main body of the furnace and its walls rest on plates of cast-iron circularly arranged and supported by numerous large cast-iron pillars, *n*.

The blast furnace is started by first heating the empty furnace by burning coke in it and then gradually charging in the ore and coke as described above. When work has once been gradually started—a process which requires some weeks—it continues uninterruptedly for several years. A certain quantity of burnt pyrites is now used, together with the ordinary iron ore.[1]

In America the production of iron in blast furnaces commenced in 1750 and developed considerably during the eighteenth century, but the most fantastic prophet could not have foreseen the immense development of the iron industry in the United States to-day.

In England the development of the iron industry was closely connected with the possibility of replacing wood charcoal by coal. The first unsuccessful attempts in this direction did not discourage British enterprise, and in 1740 A. Darby and R. Ford succeeded in replacing wood charcoal in the blast furnace by coke prepared from coal, thus increasing the daily output of each furnace considerably. The old furnaces, working with wood charcoal, were increased in size to a height of 12, 15, and even 19 metres in order to compete with the new process, but the maximum production never exceeded 1 ton per day, whilst in a coke furnace in 1800 4 tons of iron per day were produced in certain cases, and the consumption of coke was about 2 tons per ton of iron produced, whilst the consumption of wood charcoal was double and sometimes even four times that amount. The output of the blast furnaces was still further increased by improvements in the blast. Instead of leather bellows more powerful wooden bellows were employed, and then, on the introduction of the steam-engine, cylindrical blowers were proposed by Smeaton in 1768, by which means even the charcoal furnaces were able to raise their production from 300 tons in 1740 to 550 tons in 1788.

On the continent of Europe the first blast furnace using coke appeared in 1767, but was not immediately successful. In England, however, there were more than 161 blast furnaces in 1805, of which only two still used wood charcoal, and at that period England overran all the world's markets and remained for many years at the head of iron-producing and consuming countries.

This pre-eminence did not, however, remain uncontested, and a serious difficulty for England arose from the first in the refining of the cast-iron, that is, in its transformation into wrought-iron by repeated heating with wood charcoal. Attempts made in 1780 to refine the cast-iron with coal did not yield good results, but in 1783 Cort patented a refining furnace which raised hopes of the solution of this problem. In 1784 the first puddling furnace was proposed simultaneously by B. Onions and by Cort; the cast-iron was charged into a reverberatory furnace with a sand-covered hearth and heated with stirring in presence of air until gas was evolved; the stirring was continued until the atmospheric oxygen gradually removed the carbon from the cast iron in the form of carbon monoxide and dioxide, so that the mass was converted into lumps of wrought iron.

This process was jealously kept secret, but in 1800 the first drawings of puddling furnaces were gradually acquired by other countries, although the predominance of England had already been established.

[1] In the past this could not be used, as it contained 4 per cent. and even more of sulphur. The St. Gobain Company, near Vienna, in 1873 attempted desulphurisation in Perret's multiple hearth furnace, using alternate hearths for pyrites and for burnt pyrites.

Burnt pyrites may now be obtained (if it does not contain zinc or lead) with 2 per cent. of sulphur in the case of lumps or 1 per cent. in the case of smalls, and is well suited for the production of iron. Since 1902 the English ironmasters reject pyrites containing more than 2 per cent. of sulphur, whilst in Germany it is rejected if it contains more than 1½ per cent.

Powdered pyrites, however, obstructs the blast furnace, and attempts have, therefore, been made to form it into briquettes with the help of tar, peat, and limestone, which latter removes the sulphur. In other cases it is worked to a paste with lime and converted into briquettes, which, after drying, are suitable for smelting. In any case these materials very soon become pulverised at the high temperature of the blast furnace and under the strong compression of the material resting on them, and therefore cause much trouble. Attempts have, therefore, been made to work up the burnt pyrites with clay and sodium silicate (7 per cent.), baking the briquettes in gas furnaces in order to harden them, after which they can advantageously be

The carbon dioxide which is formed by the combustion of the carbon in the air supplied by the blowers is converted into CO on passing through the layers of hot carbon, and this acts on the layers of ore through which it passes and removes oxygen from the iron oxide, again forming CO_2 together with spongy metallic iron. The same reactions alternate and are repeated in each layer. At the upper mouth of the furnace the *blast furnace gases* escape. These were once burnt in the air and lost, but are to-day utilised, as they contain much CO and have considerable calorific power; their percentage composition varies between the following limits: CO_2, 8–14; CO, 20–25; H, 8–9·5; N, 55–60; O, 0·4–0·8; CH_4, 2–3; water vapour, often 5; the calorific value is 800–1200 Cals. per cu. metre. In order to utilise them they are conveyed by large iron pipes, *h* and *i* (Fig. 317), of 1·5 to 2 metres diameter to the *regenerator* for the blast (Fig. 318), and also to the boilers of the steam-engines which yield the necessary mechanical energy for the works. In some cases the gases are used in the foundry to dry the moulds and to heat the drying chambers. In order to detect leakage of the gases, which are poisonous, they are passed through calcium carbide, which with the moisture present develops acetylene, this rendering the gases odorous and at the same time giving them greater calorific value. In other works the gases are used to heat open-hearth furnaces, being previously mixed with four times their volume of coke-furnace gases; the mixture has the calorific value 1800–1900 Cals. per cu. metre and may be used advantageously in place of the ordinary producer gas employed for open-hearth furnaces. To-day, however, these gases are preferably utilised directly in gas engines, as in order to obtain 1 h.p. less than 4 cu. metres are required in this way, whilst in order to obtain the same amount of energy from a steam-engine 22 cu. metres are necessary. In 1895 Thwaite and Gardener at Glasgow and Cockerill in Belgium first used 12 h.p. gas-engines, but to-day the best results are obtained with 1200 or even 8000 h.p. gas-engines.[1] In 1902 more than 200,000 h.p. were thus utilised in Europe. At Portoferraio in the works of the Società Alti Forni Elba, about 4000 h.p. were produced in 1908 from the blast furnace gases in 1300 h.p. engines.[2] The Indiana Steel Company of Gary has sixteen blast furnaces, of which 45 per cent. of the gases are used for the production of 200,000 h.p. In 1909 there were in Germany 514 large blast furnace gas-engines generating 677,000 h.p. and using 5,000,000 cu. metres of gas per hour (use

---

used in the furnace. There are now special furnaces for desulphurising burnt pyrites, and the desulphurisation is facilitated by addition of a little manganese ore.

Charges for blast furnaces are used containing 12 to 25 per cent. of burnt pyrites, 30 to 35 per cent. of limestone, and 40 to 50 per cent. of iron ore. Cast-iron is thus obtained containing 0·02 to 0·09 per cent. of sulphur and as much as 3 to 4 per cent. of silicon.

In Italy in 1901 the Società elettro-siderurgica Camuna at Darfo (Val Camonica) attempted to use burnt pyrites in the Stassano electric furnace to make cast-iron and steel, but the results were not encouraging. In 1906 Carcano and Namias tried to utilise burnt pyrites mixed with manganese ore in the electric furnace for making different alloys of iron and manganese from spiegeleisen to 80 per cent. ferro-manganese, but, although encouraging results were obtained, they were not such as to lead to a more extended industrial use of the process.

[1] The *Cockerill engines* are among the best. The 8000 h.p. model, which is probably the most powerful gas-engine in existence, weighs, without the connections and dynamo, 750 tons, *i. e.*, about 109 kilos per effective h.p. The double angle shaft weighs 75 tons and is in three pieces. The guaranteed consumption of gas corresponds with 1910 Cals. per indicated steam h.p.-hour and 2150 Cals. per effective h.p.-hour.

The mechanical efficiency is about 89 per cent., the consumption of cooling water 50 litres per effective h.p. and that of lubricant 1·1 gram. In the first experiments with 200 h.p. engines, the consumption of gas corresponded with 3260 Cals., that of water being 100 litres and that of lubricant 18 grams.

[2] The company which owns the blast furnaces, foundry and steel works at Piombino employed before the war about 3000 workmen and annually treated 100,000 tons of iron ore from the island of Elba, which cost 8*s.* 10*d.* per ton at the mine. With a new blast furnace they also treat calcareous iron ore from Campiglia. The blast furnace gases are used to heat the blast of the furnaces, and also to drive three large gas-engines to produce electrical energy, which may also be produced by a reserve gas producer. The blast furnace produces pig iron for the foundry and consumes 950 kilos of coke per ton (1000 kilos) of cast-iron. The new blast furnace is able to turn out 200 tons of cast iron per 24 hours. A regenerative open-hearth furnace has also been projected, capable of producing up to 300 tons of steel per day. The slag from the blast furnaces is partially used in the manufacture of cement, and it is intended to granulate it and convert it into bricks. The first coke ovens were not supplied with arrangements for recovery of the distillation products, but their heat was utilised for the production of steam and power for the blowing engines of the blast furnace. They are now using new coke ovens on the system of C. Otto & Co., in which the by-products are recovered and the excess of gas is used for the production of electrical energy.

of all these gases would give 1,000,000 h.p. with a consumption of 7,500,000 cu. metres of gas per hour). In the United States in 1910 250,000 h.p. were thus generated. It is calculated that, for each ton of cast-iron produced, sufficient gas is obtained to yield 300 to 400 h.p.-hours.

For some years it has been found advantageous to inject previously dried gas into the blast furnace, as was suggested by Gayley in 1904; in case, however, this is not used in gas-engines it is necessary to dry the air before injecting it into the furnace. In the Isabella works in the United States the use of dried air raised the daily output of cast-iron from 363 to 454 tons. The air is dried by means of either freezing machines or fused calcium chloride (*see* p. 620). The advantages of dry air lie in elimination of irregularities in the working of the blast furnace caused by variation in the degree of moistness of the air, in the prevention of the dissociation of the water (with loss of heat), and especially in the removal of disturbance of the chemical equilibrium inherent to the chemical reactions of the blast furnace, such disturbance being formerly produced by the action of steam on the coal and red-hot iron. The production of 1 kilo of cast-iron requires 4,460 Cals., and with dry air in the blast furnace the temperature is kept about 200° higher, giving increased output and saving of fuel. Apart from suitable admixture of the ore with the necessary quantity of flux, the nature of the fuel is of importance. Wood charcoal was once used, but was too dear, and was then advantageously replaced by coke which, being harder, allows much larger furnaces to be used, which to-day turn out 770 tons of iron per 24 hours in America, whilst in the first blast furnaces the production was only 3 to 4 tons. For certain ores a blast furnace yielding 100 tons of cast-iron per day requires 95 tons of coke and 56 tons of limestone, and produces about 85 tons of *blast-furnace slag*, the composition and utilisation of which have been described on p. 764. These large amounts of slag are also used together with gravel for road-mending and for making cement, artificial pumice and marble, and arenolite bricks (*see* p. 746), good bricks being obtained by mixing the fine, moist, granulated slag with milk of lime, and compressing the resulting paste into bricks, which are allowed to harden in the air.

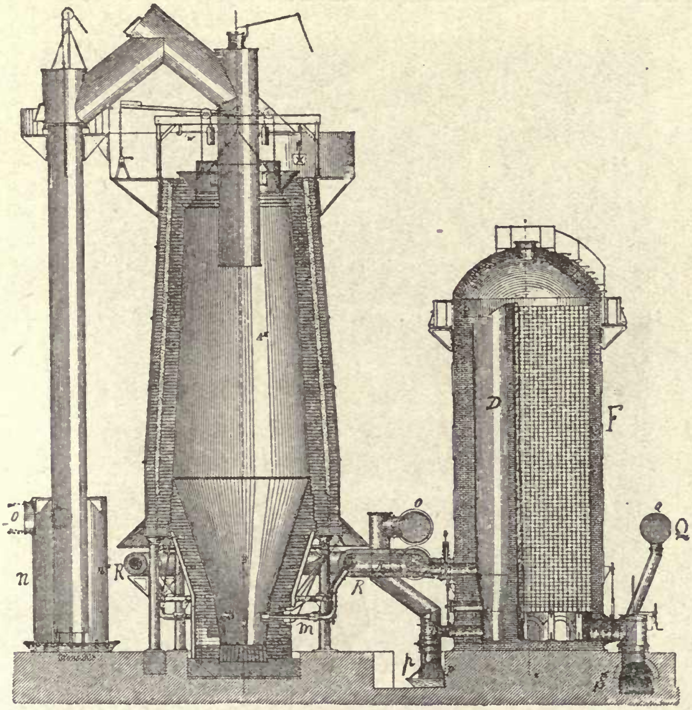


FIG. 318.

A blast furnace of the type already cited, yielding 100 tons of cast-iron per day, produces

250 cu. metres of gas per minute and utilises about the same quantity of air in the blast at a temperature of 250° to 300°. When these gases escape from the blast furnace they deposit their dust in an iron cylinder, *n* (Fig. 318), and then pass through the horizontal tubes, *o*, into *p*, which leads to the bottom of a cylindrical *Siemens regenerator* (pp. 453 and 634), *F*, as devised by Cowper (*Cowper's stove*). This is 15 to 20 metres high, and has a diameter of 6 to 8 metres.[1] The inside of the regenerator contains numerous clay cylinders of which there may be as many as 500, with a heating surface of about 5000 sq. metres, and thus the gases burn together with air which enters through the large flue, *D*, and then descend along the small passages between the cylinders, heating them strongly and finally escaping to the chimney through the flue, *S*. This furnace is heated to 900° to 1000° in one hour, and the gases are then burnt in a similar neighbouring furnace, whilst cold air enters the first furnace, passing in through the tube, *o*, from the compressor, and being heated to 600° to 800°. The hot air then passes through the well-insulated pipe, *R*, from which it is distributed to various pipes which lead it to the tuyères, *m*, inside the blast furnace.

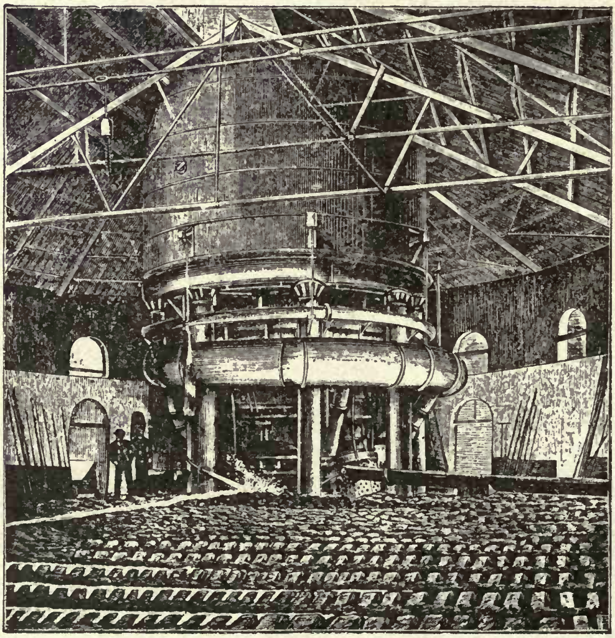


Fig. 319.

With this arrangement the temperature inside the blast furnace is 20 per cent. higher than it was before hot blasts were used. Cowper's stove has extended rapidly throughout Europe since 1865 and has led to great economy of coke, as the quantity used fell from 3 tons to 1 ton. A further economy of 5 to 10 per cent. of coke and a 10 per cent. increase of production have been achieved by previously drying the air of the blast.

The molten cast-iron is usually discharged from the furnace in the evening and in the morning, allowing it to flow whilst red hot into channels formed of earth, and directing the molten iron into numerous moulds also of earth, which are lined with sand. The cast-iron is thus obtained in bars (*pigs*) ready for further treatment. Fig. 319 shows the lower part of a blast furnace at the moment when the iron is discharged. In 1902 there were

---

[1] There have been many improvements of the various tube systems for preheating the blast, for instance, the bundles of tubes called *Calder* tubes, arranged in a suitable furnace as devised by Neilson, and those proposed by Faber du Faur in 1831, and placed in the upper mouth of the blast furnace, which are heated by the gases escaping at that point. This latter system of tubes was for a long period known as the Wasseralfinger system, from the name of the works in Würtemberg in which it was first applied, but the system devised by Alfred Cowper is the most important of all, namely, the system of applying the principle of Siemens regenerator furnaces as stated above.

93 blast furnaces in France (122 in 1906, but only 111 active in 1907, 150 in 1908, of which 106 were working and produced 11,000 tons of cast iron daily);[1] in 1910 there were 156 active blast furnaces, 26 in Belgium, 343 in England, 139 in Sweden, 11 in Italy, 14 in Canada, and 266 in the United States, in which country 340 furnaces were working in 1906;[2] in Russia in 1910, of 276 blast furnaces, only 125 were working. In 1910 there were in Germany 309 blast furnaces, 267 of them at work; each furnace had an average continuous period of working amounting to 48 weeks, and 396,000 workpeople were employed in the industry.

For many years it was believed that the abundance of CO in blast-furnace gases was caused by incomplete reaction between the iron oxide and the CO. The height of the furnaces, the temperature conditions and the pressure were all varied, but in vain. It is not actually possible to improve matters in this respect, because the reaction,

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2,$$

is reversible, and is subject to the laws of chemical equilibrium (*see* p. 64).

The relation between the CO and CO_2 cannot therefore be appreciably modified, also for the reason that there is no alteration of volume during the reaction, as 3 vols. of CO form 3 vols. of CO_2, and thus the relationship between the CO and CO_2 is independent of the pressure and constant for a given temperature (pp. 473, 474). Further, since but little heat is evolved during this reaction, the relationship is only altered to a minimal extent by variations of the temperature, and the complete reduction of the Fe_2O_3 is only partially due to the action of the CO. Nothing, therefore, remains but to utilise the gases formed in the blast furnace as completely as possible, and as a matter of fact these now constitute an important source of energy.

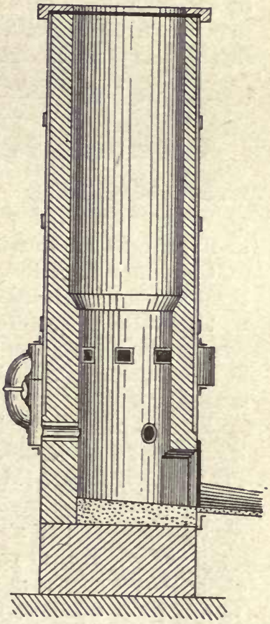


FIG. 320.

The various qualities of commercial cast-iron are prepared by remelting the crude pig iron.

Small *foundries* obtain their cast-iron from scrap iron which they charge into a furnace

---

[1] At the beginning of the nineteenth century in England wood charcoal had everywhere been replaced by coke from coal, and in 1837 G. Crane applied anthracite successfully, as had already been done in America, and obtained the first ton of cast-iron by means of hot air, but on the continent of Europe improvements were introduced more slowly. In France there was only a single blast furnace using coke until 1818 at Creusot, but another was then erected at St. Etienne. In Belgium until 1812 the greatest impulse was given to the industry by John Cockerill at Seraing, near Liége, by the use of coke and of puddling furnaces, and in 1823 he constructed a blast furnace using coke, about 15 metres high, which produced 10 tons of cast-iron daily, to the admiration of the whole of Europe. In 1838 there were 32 blast furnaces in Belgium. In Germany in 1837 90 per cent. of the iron was still produced with wood charcoal, 75 per cent. in 1850, 30 per cent. in 1860, and then, after 1870, coke was used everywhere. In Austria the first coke blast furnace was constructed in 1821. The first blast furnace in America was erected by Germans in 1809, and in 1811 there were already ten of them; the replacement of wood charcoal by anthracite was tried with complete success in 1830 by Geissenhainer, who used powerful English cylindrical blowers.

In 1837 the use of bituminous coal was tried with good results, but the use of coke only slowly extended after 1841. Scandinavia alone, with its enormous forests, has continued until to-day to work with wood charcoal.

A great improvement in iron smelting, apart from improvements in the construction of the furnaces, which are now built partly of brickwork and partly of iron, was carried out in 1829 by J. Neilson, who proposed the use of a hot blast. He succeeded in this way in doubling the output per furnace, and whilst 8 tons of coke were used to obtain 1 ton of iron with a cold blast, the consumption fell to 5 tons with a blast at 150°, and to about 3 tons at a temperature of 300°.

[2] An idea of the enormous proportions of blast furnaces is given by the following particulars as to the transport of a blast furnace in 1918 from America to India (Tata Iron and Steel Co., Sakchi). The furnace, built in 1903, was 26 metres high and 4 metres in diameter; it was provided with four Whitwell regenerators, 27 × 6 metres, with a chimney 55 × 2·70 metres and with 125 h.p. hot blasts. In 60 days it was dismantled, 90 per cent. of the firebrick being recovered. Its transport to the Panama Canal required 250 trucks.

mixed with coal. This furnace is small, cylindrical, and vertical, with an internal lining of fire clay (Fig. 320); it is called a *cupola furnace*, and air is injected below. Such cast-iron from blast furnaces as is not immediately transformed into steel is also remelted and refined in cupola furnaces, being mixed with cast-iron scrap, coke, and 2 to 3 per cent. of lime according to the quantity of silica which it contains; a more homogeneous casting is thus obtained, which is harder and has a finer grain. *Malleable castings* are obtained by heating the castings obtained in the cupola for three or four days in furnaces until they become coated with iron oxide, thus producing slight decarbonisation at the surface. In producing iron castings it is necessary to allow for the coefficient of expansion of the cast-iron, which is $\frac{1}{162,000}$ of its length for each degree, and when a casting solidifies, about $\frac{1}{100}$ linear shrinkage is allowed. The density of grey or black cast iron is 7, and that of white cast-iron 7·5.

When repeatedly heated, cast-iron increases in volume, as it becomes porous (as much as 10 per cent. increase after 100 heatings).

Cast-iron is sometimes tempered, for instance, by immersing it in oil whilst hot, and it then becomes less brittle.

The value of cast-iron which is to be used for the manufacture of steel depends considerably on its contents of silicon and manganese, because if these are present in large quantity a higher temperature is obtained in the converter and purification is easier.

By remelting in cupola furnaces either white or grey cast-iron can be obtained at will by cooling more or less rapidly. The difference between the two qualities is indicated in the Table on p. 811. Metallurgical coke is added in the cupola to the extent of about 130 kilos per ton of cast iron obtained. The cupola is heated from the commencement and an air blast is then used at 30 to 40 cm. pressure.

White cast-iron is sometimes so hard that it cannot be scratched even by the hardest steel. When grey cast-iron is rapidly cooled it is converted into white cast-iron; conversely white cast-iron, which is more difficult to melt, is transformed into grey cast-iron if slowly cooled.

Grey cast-iron has a grey lustrous aspect with granular structure and fracture, is not malleable, melts easily, and passes directly from the solid to the liquid state at 1200° to 1300°; it cannot therefore be welded, whilst white cast-iron remains pasty before melting at 1100° to 1200°. Cast-iron containing 10 to 20 per cent. of Mn is called *spiegeleisen*.

Cast-iron containing much sulphur (more than 0·3 per cent.) is of inferior quality, and in order to prevent the sulphur from the coke from passing into the iron in the blast furnace, Reusch (1902) proposed to render the slag more liquid by the addition of a little manganese ore—0·5 to 1 per cent.—but Wedemeyer (1904) maintains that desulphurised cast-iron is not obtained even when 5 per cent. is added.

A *malleable cast-iron* or decarburisation of castings to a depth of 2 cm. may be obtained, according to Ger. Pat. 213,950 of 1908, by immersing the castings in molten sodium hydroxide at a temperature of 1100°.

According to Orthey (1907) cast-iron with a maximum resistance to tension and minimum resistance to bending should contain 20 to 25 per cent. of its total carbon in the form of carbide, 0·5 per cent. of manganese, 0·2 to 0·5 per cent. of phosphorus, 1 to 1·5 per cent. of silicon, and 0·06 to 0·15 per cent. of sulphur, according to the thickness of the castings; a very pliable cast-iron which has very little tensile strength should, on the other hand, contain, according to the thickness of the casting, from 1·4 to 2 per cent. of silicon and minimal quantities of manganese, phosphorus and sulphur; good pliability and fair resistance to tension are obtained in castings of intermediate composition.

There are also special cast-irons for various mechanical and chemical uses. Thus, cast-irons which resist the action of concentrated acids (sulphuric and nitric), even in the hot, are those which are rich in silicon (10 to 16 per cent.) and are comparatively brittle; if the castings are not made with great care in the cooling they crack, owing to the great internal stresses. Ordinary molten cast-iron dissolves much ferrosilicon (up to 15 to 20 per cent. Si), but it is necessary, for the silicon to dissolve, that the cast-iron contain at least 3 per cent. of carbon. Among these special cast-irons are *tantiron* and *helianite*.[1]

WROUGHT IRON. Other qualities of iron and steel are obtained from crude pig iron by decarburising it to a greater or less extent. At one time wrought-iron was obtained in the Catalan manner by the direct action of wood charcoal on the ore under the action of an air blast.

White cast-iron is more suitable than the grey variety for the preparation of wrought-iron, because combined carbon is more easily eliminated than graphitic carbon. The decarburisation or refining may be carried out in various ways; in the *finery* or *open hearth*, by dropping the molten cast-iron through a current of air and then passing an air blast into the molten mass. The temperature is considerably raised by the combustion of the carbon contained in the cast-iron, and decarburisation is completed on the floor of the crucible with formation of a considerable amount of slag rich in iron.

At a very high temperature the greater part of the fused slag is easily separated, and when refining is finished the last residues of slag are eliminated by removing the lumps of semi-molten iron from the furnace and hammering them; at every blow of the hammer portions of the remaining slag are beaten out of the iron. From 100 kilos of crude pig iron about 75 kilos of wrought-iron are obtained.

This iron, when of the best quality, is very dear, and therefore in about 1784 the refining of cast-iron by *puddling* was started in England. This operation is conducted in reverberatory furnaces with hearths covered with slag from a previous operation. The cast-iron is continuously stirred as it gradually softens in order to bring it into intimate contact with the air and eliminate the carbon. It is heated by the direct flame of a coal furnace, and fluxes are added if necessary so that a slag rich in iron is obtained until decarburisation is complete. At the end of the operation lumps of pasty iron are obtained, because whilst cast-iron readily liquefies the wrought-iron gradually becomes pasty, and these are then hammered in order to eliminate the last traces of slag. Puddling conducted in this manner is a very lengthy operation lasting several days, and is very exhausting and dangerous for the workmen, and also very difficult. Attempts have, therefore, been made to render the operation more automatic and to effect an economy of fuel.

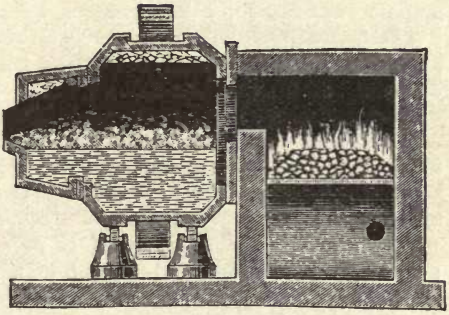


FIG. 321.

Since 1871 the problem may be said to have been solved by means of Danks' rotary furnace (Fig. 321). The fireplace is similar to those of the usual furnaces and the cylinder —where the cast-iron is melted—is formed of cast-iron plates and lined internally with refractory materials (hæmatite and bauxite). The cylinder revolves on pulleys and is turned by cog-wheels. Each charge, which consists of 35 tons of cast-iron, may be introduced in the liquid state as it is discharged from the blast furnace; 50 per cent. of fusible slag is then added in order to refine the product.

When puddling is conducted in this manner it lasts from 1 to 2 hours, and the final lumps of pasty iron are first hammered with the usual hammer and then transformed into sheets, wires, rods, etc., or directly into steel. Pernot furnaces with a circular revolving hearth were used later, and their output was double that of the Danks' furnace.

---

[1] In *Italy* 74 tons (£6,512) of helianite were produced in 1915, and 205 tons (£24,600) in 1916. The *classification of cast-irons* is still empirical, the commoner types being as follows:

	Total C Per cent.	Si Per cent.	Mn Per cent.	S Per cent.	P Per cent.
Fine hæmatite cast-irons . .	4	1·5–2·5	<1	<0·5	0·06
Cast-irons for ordinary castings .	3·5	1·5–3·5	1	0·15	<0·75–1·25
Basic cast-irons	—	<1	3	Little	1·5–4
Special spiegeleisens . . .	—	—	25	—	—
Ferromanganese	—	—	80	—	—
Ferrosilicon	—	16	—	—	—

The refining of pig iron is conducted still more rapidly and perfectly in Bessemer converters, which are also used for the production of steel, their output being very large. Whilst puddling in the primitive puddling furnace lasted several days or even entire weeks for the conversion of a few tons, 10 tons of iron are now decarburised in the Bessemer converters in 15 to 20 minutes (*see below*), the iron then containing less than 0·25 per cent. of Si, 0·2 per cent. of sulphur, and 0·5 per cent. of phosphorus.

ELECTROLYTIC IRON. This is almost pure and has assumed industrial importance only during recent years. Of the processes tried[1] the best seems to be that patented in 1910 by the ' Le Fer " Company of Grenoble. In this use is made of a rotating cathode in a neutral solution of iron salts (obtained by dissolving even cast-iron), neutrality being maintained by circulating the bath over an iron surface. Depolarisation is effected by periodic addition of ferric oxide, which expels the hydrogen deposited on the cathode; a current of 1000 amps. per sq. metre is used. Very pure iron (like Swedish iron) may be thus obtained, even directly in sheets or tubes. From any cast-iron a metal may be obtained which contains (after re-heating to eliminate gases) 0·004 per cent. C, 0·007 per cent. Si, 0·008 per cent. P (even with 1 per cent. P in the original cast-iron). With 1000 amps. per sq. metre, 2 tons of iron are obtained per kilowatt-year.

The freshly deposited metal is brittle owing to internal stresses and to occluded hydrogen (0·45 per cent.), but on re-heating greatly improves in quality, although in general it corrodes more easily than ordinary iron, possibly in some cases on account of the presence of traces of ferrous chloride (0·02 per cent. Cl). The unheated metal exhibits, on micrographic examination, a homogeneous acicular structure similar to that of martensite, but such structure disappears entirely on re-heating for 2 hours at 900° in magnesia (and after immersion for 10 minutes in a salt bath). Tubes 4 metres long, 100 to 200 mm. in diameter, and 0·1 to 6 mm. thick are now made, with a breaking tensile stress of about 31 kilos per sq. mm. and an elongation of 40 to 42 per cent.

Electrolytic iron serves well for making the rods for autogenous welding, is well adapted for making electrical machines owing to its low hysteresis, its high permeability, and its regular thickness, a saving in weight of 33 to 44 per cent. in transformers and of 50 per cent. in the capacity or power of alternating motors for equal temperature and space occupied; with continuous current machines, 16 per cent. of metal may be saved. For smelting purposes it is not inferior to Swedish iron, and has the advantage, when crude, of being easily broken for fusion.

The cost of electrolytic iron depends on that of electrical energy. With a current density of 500 amps. per sq. metre (instead of 1000), the voltage falls to about one-half and the output per kilowatt-year is almost doubled (4 tons instead of 2), and is hence advantageous where energy is costly. At 0·1*d*. per kilowatt-hour, the energy would cost £1 14*s*. per ton, the cast-iron (assuming 10 per cent. loss) £4 per ton, and labour, maintenance, taxes, sinking fund, interest on capital, etc., would bring the total cost to about £8 per ton.

STEEL is distinguished from cast- and wrought-iron by the quantity of carbon which it contains (this being 0·2 to 2·3 per cent., preferably from 0·5 to 1·5 per cent.) and by its property of acquiring a *temper*, that is, of becoming greatly hardened and losing its elasticity when heated to about 900° and rapidly cooled in water, oil, etc.[2] Steel differs from cast-iron by its capability of being welded on to itself when heated. It has a very fine

---

[1] The first sample was obtained by Klein in Petrograd in 1860 by electrolysing a solution containing 5 per cent. of $FeSO_4$ and 5 per cent. of $MgSO_4$, a current of 0·1 to 0·2 amp. per sq. dm. being used and the bath being gradually neutralised with $MgCO_3$. In 1900 E. Merck patented a process, in which concentrated $FeCl_2$ solution was electrolysed at 70° with a current density of 3 to 4 amps. per sq. dm. Burgess and Hambuechen in 1904 electrolysed a solution of ferrous ammonium sulphate at 30° with a current density of 1 amp. per sq. dm. Foerster electrolysed faintly acid ferrous sulphate solution at 95° with a current density of 2 amps. per sq. dm. In 1907 Cowper Coles patented the electrolysis of a 20 per cent. solution of iron sulphocresylate, an attempt being made to prepare seamless tubes directly by using as cathode a revolving cylindrical core (as in Elmore's process for copper tubes). In 1909 Fischer, Langbein and Pfanhauser took out various patents, Ger. Pat. 212,994 describing the electrolysis of highly concentrated solutions of $FeCl_2$ and $CaCl_2$ at 110° with 20 amps. per sq. dm.; the iron sheets thus obtained are irregular and must be repeatedly rolled.

[2] The theory of tempering is not yet complete and various hypotheses have been proposed to explain this phenomenon. It is probable that the action of the liquid in which the hot steel is immersed is due to a more or less rapid supply of oxygen and other more or less reducing gases, which penetrate the steel to a greater or less extent, transforming the *cementite* (iron carbide) into *ferrite* and separating carbon.

grain which is the finer the better the quality. Its structure becomes apparent on immersing steel in HCl. It is more or less hard and more or less elastic according to its composition and the way in which it has been treated. It melts more easily than wrought-iron, at 1300° to 1800°. Its hardness is diminished on heating it for a long time, and on altering the temperature it assumes colours varying from reddish-yellow to iridescent blue (soft steel, watch springs, knife blades, etc.). During cooling hot steel contracts to some extent and then suddenly expands; this phenomenon may be repeated several times.

Steel obtained directly from the ore is not much used. Almost all steel is to-day prepared by the Bessemer process, which was started in 1855 and became general later. Since this process became known, the Martin (open-hearth) process and various others have been introduced; these we shall briefly describe.[1] A good steel contains less than 0·07 per cent. of sulphur and less than 0·12 per cent. of phosphorus.

MANUFACTURE OF STEEL AND MOLTEN OR HOMOGENEOUS WROUGHT-IRON by the Bessemer process. The greatest advance in the metallurgy of iron was achieved in 1855 by the invention of Henry Bessemer of Sheffield, who produced enormous quantities of iron and steel rapidly and perfectly in his *converter* (*see below*). In the Bessemer process a strong blast of compressed air is forced through the molten cast-iron contained in a pear-shaped iron receiver (*converter*, Fig. 322) lined internally with siliceous fireclay. A very high temperature is maintained not only by the decarburisation of the cast-iron, that is, by the combustion of the carbon, but more especially by the combustion of the silicon which is always contained in cast-iron and is also supplied by the converter lining. The silicon, manganese, and a part of the phosphorus are eliminated in the form of slag, whilst the decarburised iron remains as a liquid and therefore forms a highly homogeneous product. The Bessemer converter, which is 5 metres high, has a capacity of 10 tons of cast-iron. It can be revolved on two pivots by means of the cog-wheel, *H*, actuated

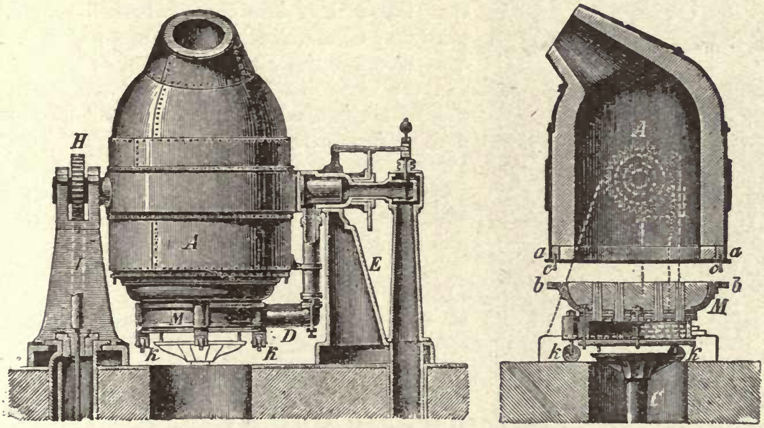


Fig. 322.

---

[1] In ancient times and until the Middle Ages, the preparation of steel was greatly dependent on chance and it could not be obtained with certainty as required. Agricola in 1550 and Biringuccio describe the reliable preparation of steel by cementing wrought-iron in a bath of molten cast-iron obtained directly from the ore, by heating, stirring, and adding wrought-iron until the cast-iron itself became pasty and refined, and the whole mass was thus converted into steel. In this process there was, however, much loss, which sometimes exceeded 50 per cent. of the metal treated. In the eighteenth century another process for preparing steel was perfected, namely, the true *cementation* process. In this process the wrought-iron was converted into steel by heating it in presence of powdered charcoal until it softened, and then treating it in such a manner that it absorbed the exact quantity of carbon required. This process was used in Piedmont in the seventeenth century and afterwards in England, and was carefully studied and perfected by Réaumur in France in the eighteenth century by preparing suitable cementing powders and constructing suitable furnaces in order to assure a successful result for each operation. In 1740 Huntsman discovered a method of obtaining cast, refined, homogeneous steel in a single operation by heating welded or cemented steel with pure coke in fireclay crucibles in furnaces in an air blast. This process was kept secret until the commencement of the nineteenth century, and *cast-steel* was only supplied by England.

by a hydraulic piston, *I*, and thus when the operation is finished the converter can be inverted in order to discharge the molten iron or steel. At the base of the apparatus an internally perforated box, *M*, is held by hydraulic pressure and subdivides a powerful jet of compressed air which passes in through the tube *E* at the right and then enters through the tube *D*, supplied with a regulating valve.

The converter is charged with molten cast-iron by inclining it at a suitable angle and is then turned into an erect position, a jet of air being immediately passed through the liquid metal. Through combustion of the Si, Fe, Mn, C, and P the temperature is greatly raised, and for the first 3 or 4 minutes sparks only escape at the mouth and are followed by a small, and finally by a large, flame accompanied by sparks, explosions, and brown smoke. The flame (Fig. 323) is continuously observed through a spectroscope in order to note its character. After 7 or 8 minutes the flame becomes brighter, the explosions diminish, and to the spectra of sodium and potassium which characterise the first period the spectrum of carbon monoxide is added during the second period, which lasts for 8 to 10 minutes. This carbon monoxide is formed from the ferrous oxide and carbon in the iron. After all heaving motion of the liquid iron has ceased and the flame has become brighter but smaller, all the green spectral lines of CO disappear and a continuous spectrum is obtained, whilst many sparks are still ejected. This is a sign that the carbon has been entirely oxidised. This third period, which is the period of refining, lasts from 8 to 10 minutes. Decarburisation is then complete and the operation is finished. If molten wrought-iron with less than 0·6 per cent. of carbon is required, nothing further is needed but to pour the contents of the converter into suitable moulds. If, on the other hand, steel is required, a given quantity of manganiferous cast-iron (spiegeleisen) and other iron containing a definite percentage of carbon (or even a definite quantity of coke) is then added to the molten mass, which is stirred for a few minutes by means of the air blast, after which the steel is ready to be poured into suitable moulds.

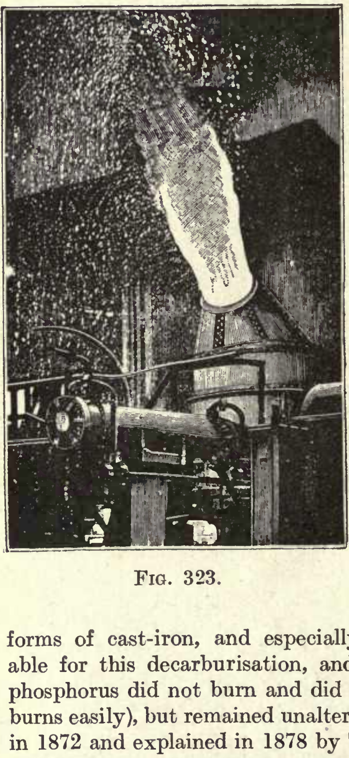


FIG. 323.

40 to 60 charges, each of which weighs 10 to 20 tons, can be treated per 24 hours in each converter. It is thus clear that enormous quantities of iron and steel can be produced in a short time with a few Bessemer converters. Converters holding 25 tons are now in use.

From the earliest days of the application of the Bessemer process it had been found that many forms of cast-iron, and especially those containing much phosphorus, were not suitable for this decarburisation, and formed a faulty and unserviceable iron because the phosphorus did not burn and did not pass into the slag (although it is an element which burns easily), but remained unaltered in the iron. This curious fact was studied by Snelus in 1872 and explained in 1878 by Thomas and Gilchrist, who showed that the phosphorus could not be transformed or separated in the slag as calcium phosphate, because the internal lining of the converters contained much silica, and therefore rendered the metallic bath markedly acid, so that the acid phosphates or phosphoric acid formed were easily reduced by the iron; this therefore finally contained all the phosphorus.

Having thus explained the reason for this phenomenon, Thomas and Gilchrist introduced the replacement of the acid lining of the converter by a *basic lining* composed of powdered magnesia and dolomite worked to a paste with a little tar and compressed, and added if necessary to each charge 10 to 15 per cent. of quicklime and flux, calculated on the weight of cast-iron containing 2 to 3 per cent. of phosphorus. In this way all the phosphorus separates in the form of calcium phosphate in the slag, which is so rich in phosphates that after being finely powdered it forms an excellent chemical manure able to compete advantageously with superphosphates. In 1907 2,600,000 tons of *basic slag* were produced (*see* pp. 648, 662); in 1911 the world's production of the slag was 3,485,500 tons (2,160,000 in Germany), and in 1913 4,500,000 (2,250,000 in Germany). On the average 1 ton of the slag is obtained per 4 tons of steel.

Treatment by the basic process is conducted in the same manner as by the acid process, and dephosphorisation occurs in 4 or 5 minutes during the last period when the flame has almost or quite disappeared. By suitably inclining the converter the slag alone is poured into iron trucks and a calculated quantity of iron containing a known percentage of carbon is then added to the remaining metal in order to obtain steel in the usual manner. When this is thoroughly molten it is poured into moulds (*ingots*) in which it solidifies. The world's production of steel by the Thomas-Gilchrist process was only 3000 tons in 1879, but rose to 1,000,000 tons in 1885, and in 1895 it had reached 4,000,000 tons, of which about one-half was produced in Germany; in 1907 10 million tons of Thomas steel were produced throughout the world. By the basic process cast-irons containing 2 to 3 per cent. of phosphorus are treated, whilst by the acid process cast-iron containing 2 to 3 per cent. of SiO_2 may be employed.

OPEN-HEARTH STEEL (MARTIN STEEL). In 1865 the brothers Martin prepared steel by melting about 75 per cent. of cast-iron in a reverberatory furnace with the necessary quantity of wrought-iron to obtain exactly the required amount of carbon. The *Martin* or *open-hearth* process was considerably improved by the use of *Siemens'* regenerative furnaces (pp. 453, 634), as with their help the temperature of molten iron was easily obtained, whilst without them the production of this temperature was very difficult. In the original Martin process, an acid (siliceous) hearth was used; but a basic lining was afterwards employed, with addition of lime if necessary, and in this way a phosphatic slag similar to that obtained by the Thomas-Gilchrist process is produced.

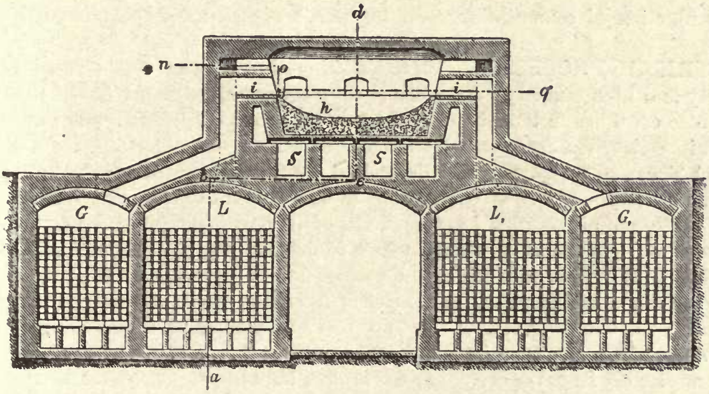


FIG. 324.

Each charge consists of 10 to 20 tons and in certain cases even 50 tons, and the process lasts from 8 to 10 hours. Steel, and more especially wrought-iron of superior quality to that obtained by the puddling process, are obtained.

The open-hearth process also presents the advantage that old iron and steel scrap may be employed, and is also suited to the direct production of steel from the ore by starting, for instance, from 60 per cent. of cast-iron, 20 per cent. of scrap iron, and 20 per cent. of ore. For these reasons the open-hearth furnace has now everywhere displaced the Bessemer converter almost completely, as in England and America, where the ores are very rich in phosphorus and not suitable for the Thomas converter.

In Fig. 324 a modern type of open-hearth furnace with the corresponding Siemens regenerator is shown in section. The path of the hot gases and the recovery of the heat are exactly analogous to the arrangements in glass-melting furnaces, described on p. 635. Open-hearth furnaces have recently been successfully heated by means of blast-furnace gases mixed with tar. A tilting furnace (Talbot) has also been used with advantage for separating the slag and discharging one-third of the molten product, which is then re-utilised with fresh cast-iron and ore (continuous process). The Talbot furnace (producing 120 to 150 tons per day) lends itself especially to the re-refining of steel, since the silicon and part of the phosphorus may be easily eliminated. The crown of the furnace lasts

15 to 20 weeks. The refining is completed in the Siemens-Martin furnace. A fixed furnace of 60 to 80 tons, with four charges per day, gives an output 15 to 30 per cent. above that of the Talbot furnace.

Whilst in 1886, in the United States, 91 per cent. of the steel was produced by the Bessemer process and 9 per cent. by the open-hearth process, in 1902 the proportions were 65 per cent. by the former and 35 per cent. by the latter. In England in 1866 the proportions of Bessemer and open-hearth steel were 69·5 per cent. to 30·5 per cent., whilst in 1895 they were 47 per cent. to 53 per cent. In Germany in 1902 69·5 per cent. of Bessemer steel and 30·5 per cent. of open-hearth steel were produced.

CAST STEEL or **CRUCIBLE STEEL.** This is a steel of very high quality which is used for heavy guns, turrets, tyres and axles of wheels, etc., and is obtained by melting open-hearth or Bessemer steel in refractory crucibles in furnaces similar to those of glass furnaces. The molten steel is then poured into moulds to form ingots.

CEMENTATION STEEL. This is obtained by heating bars of good, malleable iron, packed in nitrogenous matter or powdered wood charcoal.

Large bundles of these iron bars, weighing 10 to 12 tons, are covered with wood charcoal and packed into furnaces heated to a bright red heat by direct flame for 8 to 10 days. As the carbon penetrates slowly into the outer layers of the bars cementation steel is obtained, but its composition is not very homogeneous. The cooling lasts from 4 to 5 days.

The production of cementation steel by means of calcium cyanamide has now been proposed.

ELECTRICAL PROCESSES. Electrically produced steel has the advantages of great purity and high tenacity even when it contains one-third more carbon than ordinary steel. It also contains no blow-holes and has a very high contraction and limit of fusion.

The various electrical furnaces for steel production may be grouped under the following heads. (1) Those in which the mass is melted by heating the outside of the containing vessel: The *Girod furnace* is of this type. It uses current at 60 volts, produces a very pure steel and costs about £800 for a capacity of 10 tons in 24 hours; Girod plant commenced work at Ugine in 1910 which utilises 22,000 h.p. for the production of 50 tons of steel per day. (2) Furnaces in which the mass is melted by means of the resistance which the iron itself offers to the passage of the electric current and the corresponding development of heat; the *Gin furnace* is of this type and was applied at Plettenberg, and also the *Keller furnace*, which has been installed at Livet, where cast-iron and steel are produced by its means directly from the ore. For the production of 100 tons of steel per day 9750 h.p. are required at the furnace electrodes. (3) Furnaces in which smelting is effected by the heat produced by induction currents through the mass to be melted: these were proposed by Ferranti and applied at the works of Schneider at Creusot in France, but the *Kjellin furnace* (U.S. Pat. 682,088) has been still more successful, and finally yielded the best technical and economical results. (4) Melting is produced by the heat of the electric arc: the *Héroult*, *Stassano* furnaces, etc., belong to this group. This process was tried very often at first on a small scale and finally on a large scale at Darfo in the province of Brescia, rich iron ore being mixed directly with coal and suitable fluxes in specially contrived electric furnaces, in which an electric arc 1 metre long was produced, not through the mass, but round its surface, by means of an alternating current of 2000 amps. at 70 volts. The practical results were not good. Stassano obtains better results by working directly with cast-iron to obtain special steels, charges of 2 tons being used.

The *Héroult process*, which has been advantageously adopted since 1901 in certain large French works, has been more successful; in this process the molten cast-iron as it proceeds from the blast furnace is at once submitted to the action of the electric current between two large carbon electrodes. The necessary electrical energy may be produced from the gases of the same blast furnace, by which means a h.p.-hour costs less than 0·2*d*. and the steel has a value of about £4 per ton. In 1906 a plant was also erected in the United States. A Héroult furnace for the production of 10 tons of steel per twenty-four hours costs about £1200. Nowadays the Héroult furnace predominates in all countries, even for large charges (25 tons).

A mixture of cast- and wrought-iron in suitable proportions is treated without carbon electrodes in a furnace in which the molten steel replaces the secondary coil of an ordinary transformer, the current intensity being higher and the voltage lower, An electric furnace plant for producing steel directly from the ore, as used in 1910 in Sweden and also in California (*e. g.*, by the Shasta Iron Co.) is shown diagrammatically in Fig. 325. The ore used was pure magnetite (89·4 per cent. Fe_3O_4, 7·3 per cent. Fe_2O_3, 0·10 per cent. MgO, 0·10 per cent. MnO, 2·4 per cent. SiO_2, 0·011 per cent. P, 0·009 per cent. S) and the limestone employed as flux contained 1·2 per cent. SiO_2, 0·5 per cent. Al_2O_3, 1·1 per cent. MgO, 0·2 per cent. FeO and 53·8 per cent. CaO (equal to 98 per cent. $CaCO_3$). The cupola furnace, *m*, with air blast receives the charge of ore mixed with flux which is pre-heated by the hot gases from the furnace and is led by the pipe, *e*, to the large iron hopper *b* ; from this it is removed by the tip mounted on the truck, *g*, and emptied into the mouth, *h*. Alternately with this charge wood charcoal (92 to 94 per cent. C.) is introduced from the hopper *c*. The molten iron formed in the zone of combustion, *k*, where the air blown in at *l* arrives, and in the zone of reduction, flows into the electric furnace, *S*, beneath, 6 electrodes, *pq*, dipping into this. In some of the Swedish furnaces the hot furnace gases are injected by a fan against the cupola, *n*, of the electric furnace to cool it and prevent it from melting.

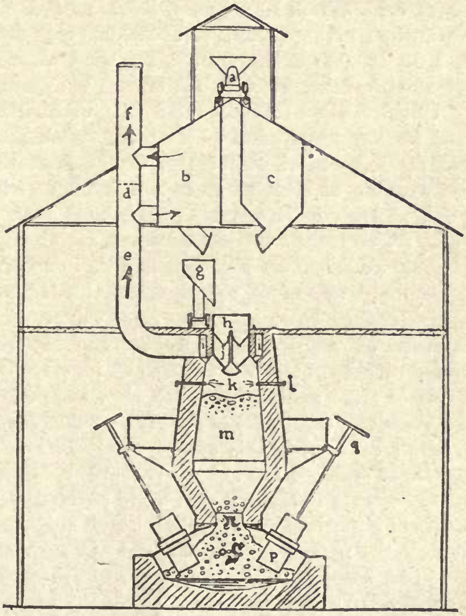


FIG. 325.

With a current of 7000 amps. at 37 volts, 300 kilos of wood charcoal and 6 kilos of electrodes are consumed per ton of cast-iron. The fuel consumption in electric furnaces is about one-third of the usual amount with air blast. In California an electric furnace showed a consumption of 0·25 h.p.-year for 1 ton of cast-iron and a further expenditure of £3.

In an electric furnace at a French works steel was obtained with 0·45 to 0·50 per cent. C, 0·009 per cent. S, and 0·008 per cent. P, with an energy consumption of 275 kilowatt-hours per ton of steel and of 18 mm. of electrode per hour, 4 electrodes of 400 × 400 mm. section being used (costing £1 8*s.* per 100 kilos); the total cost was thus 3*s.* per ton of steel, with continuous working.

In a Girod electric furnace making steel from cast-iron scrap and turnings, the consumption was 700 kilowatt-hours (for an 8 to 12 ton furnace, or 900 kilowatt-hours for a 2 ton furnace) and 13 to 15 kilos of electrode. The dolomitic brick lining of the furnace and the siliceous or chamotte brick used for the arch of the electric crucible last for 40 to 50 charges and cost 3*s.* to 4*s.* per ton of steel produced. A good lining is obtained from good magnesite or dolomite, with basic slag and tar.

Electric furnaces are especially convenient for making special steels, especially when charges of 15 tons are used. For ordinary steels they compete with the old processes only when all the factors (cost of energy, ore, etc.) are exceptionally favourable. A continuous supply of energy at less than £2 per h.p.-year is necessary.

The electric furnace is convenient also for refining highest quality steels, since it gives good desulphuration and good dephosphorisation even when very impure, and hence cheap, raw materials are used. Further, combination with converters of an electric furnace to complete and improve the refining accelerates working, and may increase the output even of blast furnaces. In such case refining in the electric furnace consumes only 100 to 150 kilowatt-hours per ton : the molten steel from the Bessemer converter is poured into the electrode furnace already containing a layer of lime or iron ore. This procedure yields an oxidising and dephosphorising slag, which is eliminated, the steel being then covered with carbon until the desired degree of carburation is effected. Finally a second portion of strongly basic slag is added to act as a desulphuriser.

To obtain refined steel from scrap steel, new electric furnaces are used to carry out the fusion in 4 hours with a consumption of less than 500 kilowatt-hours. In general the electric furnace is advantageous (assuming energy at £2 to £2 8*s.* per h.p.-year to be available) when very high temperatures are required; otherwise producers are best. When mere refining of the molten steel is carried out in the electric furnace, the cost in only 6*s.* to 8*s.* more than with the open-hearth furnace. The cost of production of 1 ton of steel by the basic open-hearth process is £3 16*s.* to £4; by the acid open-hearth process £4 4*s.* to £4 8*s.* and by the Kjellin process only £3 12*s.*, the consumption of energy being 830 to 1040 kw.-hours per ton of steel, whilst by the Héroult process it is 720 to 1100 kw.-hours, or 3400 kw.-hours for the production of 1 ton of cast-iron from the ore. The current yield is about 65 per cent.

In 1910 there were under construction throughout the world 40 electric furnaces and actually working 67. Of the total of 107, 29 were of the Héroult type, 14 Kjellin, 13 Stassano, 17 Girod, 15 Röckling-Rodenhauser, *i. e.*, 32 induction furnaces and 72 with electrodes. In 1913 there were quite 200 electric furnaces working (39 per cent. Héroult, 16 per cent. Girod, 10 per cent. Röckling-Rodenhauser, 6 per cent. Kjellin, and 5 per cent. Nathusius), giving an output of 200,000 tons of steel; in 1915 the output was 244,000 and in 1916 490,000 tons. Only 1 per cent. of the steel production in Germany is made in the electric furnace (electrical energy is expensive).

USES AND PROPERTIES OF VARIOUS TYPES OF STEEL. Steel is to-day used for the preparation of the most varied articles; for armour-plates of ships, for large and small parts of machinery, for guns, rails, needles, watch springs, etc.; altogether the working of steel presents a marvellous example of the increased values which this metal, so truly indispensable to mankind, acquires. Whilst ordinary iron is worth only £2 to £2 8*s.* per ton, when transformed, for example, into watch springs, it acquires a value of about £800,000 per ton, that is 5 times the value of an equal weight of gold. Iron is no longer only the most useful metal, but it is the one which when treated by man is able to acquire the highest degree of value. The nature of iron and steel may not only be modified by physical and mechanical treatment, by puddling and melting to the most varied degrees of temper, but also by its chemical composition and by the addition of small traces of other substances which alter the properties of soft iron very greatly. Tungsten, molybdenum, chromium (1 per cent.), manganese (up to 8 per cent.), etc., increase the hardness of steel considerably and render it suitable for special purposes. *Manganese* acts as a species of antidote against the bad effects of phosphorus and sulphur; *nickel*—up to 6 per cent.—renders it tougher and more resistant to shock. We have already seen how even traces of impurities such as phosphorus, sulphur, and more especially of combined nitrogen, modify the nature of iron and steel to such an extent as to render it unserviceable for practical use if they exceed 0·2 per cent. of sulphur, or 0·1 per cent. of phosphorus. *Vanadium* (0·5 per cent.) and *chromium* (up to 1 per cent.) increase the resistance to fracture and to tension (from 34 to 61 kilos). In pearlitic steels containing up to 1 per cent. of *nickel-vanadium* the breaking strain is increased, whilst above 1 per cent. it is diminished; the same may be said of *mangano-vanadium* and of *siliceous steels*, but brittleness in a direction perpendicular to the lamination is not corrected. *Vanadium* for steel-working purposes costs £2 8*s.* per kilo. Excessive quantities of carbon and manganese render steel very brittle. *Tungsten*—6 to 9 per cent.—(and more particularly if 5 to 6 per cent. of *chromium* is also added) maintains the hardness of steel even at a high temperature (*rapid tool steel*).

Molybdenum (4 to 5 per cent.) also yields rapid tool steels, but these are less valuable than the tungsten steels, as they are more brittle. *Titanium* steel containing not more than 1·5 per cent. is very compact and has a fine grain. *Silicon* renders steel hard and brittle, and if 5 to 15 per cent. is added, it can be worked only in the cold, not on heating.

The steels which offer the greatest resistance to shock are those which contain 0·25 to 0·30 per cent. of carbon and a high percentage of nickel (up to 32 per cent.) or manganese; they possess, however, very little elasticity. They are very hard, and if they contain 2 per cent. of chromium become still harder; they are worked with an emery wheel, for example, in the manufacture of valves for petrol engines and buffers for railway wagons, which are subjected to continual shocks. Hard steels with a very fine grain and very susceptible to high temperatures are obtained by the addition of minimal quantities of vanadium (0·2 to 0·6 per cent.) or even better of chromium and nickel as well. They are thus very uitable for parts of machinery which are subjected to shocks and to rapid velocity changes, such as the cogs of automobiles, shafts of pulleys, etc. Silicon steels are very elastic and offer great resistance to tension. Steels containing 0·3 per cent. of carbon and 5 to 6 per cent. of nickel are the most suitable for tempering, and if they also contain manganese and chromium they become slightly tempered even in the air (*self-tempered steels*). Steels for armour-plates, for large projectiles and for transmission shafts containing 6 per cent. of nickel and 0·2 per cent. of vanadium, are tempered in water, or if they contain, for example, 4 per cent. of nickel and 1 per cent. of chromium, also in oil. Steels which contain more than 0·35 per cent. of carbon have to be reheated after tempering (as otherwise they remain too brittle), and they thus acquire great elasticity and resistance to fracture.

The various types of steel may be recognised without chemical analysis by the *form of the sparks* which they produce when heated to redness and hammered in a powerful current of air or when exposed to the action of an emery-wheel revolving at high speed. In this latter case by varying the pressure or nature of the emery-wheel the colour and luminous effect of the sparks are modified, but their characteristic formation does not change. In Fig. 326 the bundles of sparks from various types of steel are shown. *a* represents the sparks from forged wrought-iron, consisting of a bundle of straight lines more luminous in the centre than at the extremities and without ramifications or stars. *b* and *c* show those from soft steel and tool steel respectively, and the presence of more or less carbon is shown by the formation of a number of larger or smaller luminous stars formed of short rectilinear ramifications, which are further ramified in turn in the case of steels containing much carbon, *c*. Chrome tungsten steel for high-speed tools forms very short sparks with stars of a dark colour, because both tungsten and molybdenum become red hot only at very high temperatures. Thinner dark red rays are also observed and thicker rays of a brick-red colour. The latter are completely absent in steel containing tungsten only. The spark bundle from manganese steel, *e*, is characteristic; the rays show few sparks, but these are very highly ramified, so that they almost resemble leaves of which the extremities are united by luminous spheres. High-speed chrome steels, *f*, show long sparks, large in the middle, and of a dark red colour with a few stars. Nickel steel shows a similar effect to ordinary steels, *b* and *c*.

FIG. 326.

a. Wrought iron. *b*. Soft steel. *c*. Tool steel. *d*. Chrome tungstein steel. *e*. Manganese steel. *f*. Rapid tool steel.

FERROSILICON. This may be considered as a true alloy of iron and silicon with traces of carbon, and is used, as also is *ferromanganese* containing 30 to 80 per cent. of Mn, for purifying molten iron. Both of these substances are now almost exclusively prepared in electric furnaces, starting from iron ores with addition of coke and of manganese ores in the case of ferromanganese and spiegeleisen (Ger. Pat. 147,311) or of quartz in the case of ferrosilicon. The latter is obtained by reducing the powdered siliceous slag from the open-hearth and Bessemer processes in the electric furnace (U.S. Pat. 712,925), or it may be obtained from burnt pyrites in presence of silica. Ferrosilicon is poisonous because it evolves PH_3, AsH_3, and SiH_4 from its impurities in presence of moisture; it has also been known to cause explosions.

In *England* low ferrosilicon with 15 per cent. Si is obtained directly in blast furnaces, while that with a high proportion of silicon (up to 95 per cent.) is obtained only in electric furnaces in France, Austria, Sweden, etc., and has now replaced the lower qualities in the preparation of the best kinds of steel, at the same time increasing the dangers, since ferrosilicon containing much silicon (50 per cent.) is very porous and easily gives sudden evolution of gas, and thus causes serious explosions and poisoning. For this reason, transport of such ferrosilicon on passenger ships is prohibited, fifty persons once being poisoned, two fatally, by breathing poisonous gases (PH_3, AsH_3, and C_2H_2) liberated in this way. In any case contact with moist air should be prevented.

Ferromanganese costs from £16 to £24 per ton according to the percentage of manganese. Ferrosilicon containing 10 per cent. of Si costs up to £160 per ton, and when it contains 20 per cent. of Si, it costs more than £180; in 1909 a European syndicate was constituted regulating the production and prices. England imports 4000 tons per annum.

The importance assumed by these iron alloys is shown by the continued increase in the production.[1]

MICROGRAPHY OF IRON AND STEEL

The initial work of Sorby in 1867, who first evolved a method of studying a polished section of a metal micrographically, as had already been very successfully achieved in petrography, was quickly followed by other special studies by Martens and Wedding on wrought- and cast-iron, and in 1883 and 1894 by the important work of Osmond and Werth on steel. After that time metallographic studies increased in number and were notably added to by Guillemin (alloys of copper, bronze, and brass), Charpy (brass and anti-friction metal), and more particularly by H. Le Chatelier, who brought physico-chemical speculations to bear on these studies and showed their full industrial importance. The microscopic examination of the carefully prepared and highly illuminated surface is undertaken, not by transmitted, but by reflected light, assisted by microphotography, a suitable camera being added to the microscope. The etching of the polished surface is carried out by the process indicated on p. 515, but more especially to-day by means of certain solutions which colour one or other of the components of the wrought- or cast-iron or steel in a characteristic manner. Hilpert and Colver-Glanert (1910) obtained sharper etchings than those given in the ordinary way (by sulphuric or hydrochloric acid, etc.) by immersion of the polished surface in saturated aqueous sulphurous acid as free as possible from sulphuric acid; on withdrawal from this solution the surface is immediately washed rapidly in water, dipped into alcohol and then allowed to dry.

The theoretical researches of Roozeboom on solid solutions have found brilliant practical application in the study of alloys and of more or less highly carbonised iron. On pp. 516 *et seq.* we have already studied the phenomena which occur when a metallic alloy is slowly cooled, and have also explained graphically the meaning of the absolute and relative eutectic points by determining the chemical and microscopic composition of the substances separating at these points. The micrographic examination of wrought- and cast-iron and steel has led to the study and identification of substances which are characteristic of the various types of steel, etc.

In the alloys of iron and carbon (wrought- and cast-iron and steel) one or more of the following substances have been found micrographically according to the quality: **Ferrite, Graphite, Cementite, Pearlite, Martensite, Austenite,** etc., the properties of which we shall discuss later.

If chemically pure (electrolytic) iron is melted and then allowed to cool slowly the

---

[1] **Ferrosilicon.** The world's consumption in 1908 was 30,000 tons (one-half in the United States and 15,000 tons in Austria and France together), and in 1910 60,000 tons.

The *price* in Europe in 1910 was less than £2 per ton.

In 1911 *France* exported 3660 tons (same in 1910).

For *Italy* the statistics are (tons):

	1910	1911	1912	1913	1914	1915	1916	1917
Production .	1692	1809	2826	4700	3120	4538	9180 (£193,978)	—
Importation .	511	155	—	—	100	—	—	237

Ferrovanadium. The United States exported 274 tons in 1913, 349 in 1914, 386 in 1915, and about 700 in 1916.

Ferromanganese. England imported 14,663 tons in 1909, and 33,350 (£170,600) in 1910, the exports being of the value of £893,080 in 1909, and £1,136,280 in 1910.

France imported 6800 tons in 1911.

Italy produced 4200 tons in 1910, 6482 in 1911, 1119 in 1914, 3655 (£69,670) in 1915, and 12917 (£423,020) in 1916.

The *United States* in 1910 produced 350,000 tons and imported 140,000 tons (at £8 to £8 16s. per ton).

Ferrochromium usually contains 50 per cent. Cr. The world's production was 3000 tons in 1909.

France exported 6470 tons in 1911.

Ferromolybdenum. World's production 1000 tons in 1909.

cooling curve shows a break at about 1600° and then descends again regularly until there is another break at 890°, and finally a further break at a temperature of 770°. The two last points are indicated in the diagram (Fig. 327) by the letters *G* and *M*. At *G* the iron suddenly changes its thermo-electric properties, and above *M* the iron is non-magnetic, whilst is is magnetic below that temperature.

By means of the same criteria which were used in producing the diagram of the metallic alloy on p. 516, one may also follow that of Fig. 327, which refers to the various alloys of iron and carbon; on the axis of the abscissæ percentages of carbon are indicated, and on the axis of the ordinates the temperatures corresponding with various eutectic points. The names of the substances which separate in the various zones during gradual cooling are written in the diagram, with variation of the types of steel or cast-iron and various contents of carbon. In the case of a steel containing 0·35 per cent. of carbon the points *G* and *M* coincide at *O*, and with increase of the carbon this *double point* or critical point is lowered along the line *OS* down to 0·86 per cent. of carbon. Steel containing less carbon solidified at higher temperatures mainly separates *martensite*. Again, as the carbon rises from 0·86 to 2 per cent. the critical point is found along the line *SE* and there is separation also of *cementite*. The gradual transformations which may be caused follow in the order: austenite ⟶ martensite ⟶ troostite ⟶ sorbite ⟶ pearlite, although Kurbatow (1909) has shown that austenite passes, on the contrary, through troostite into sorbite, etc.

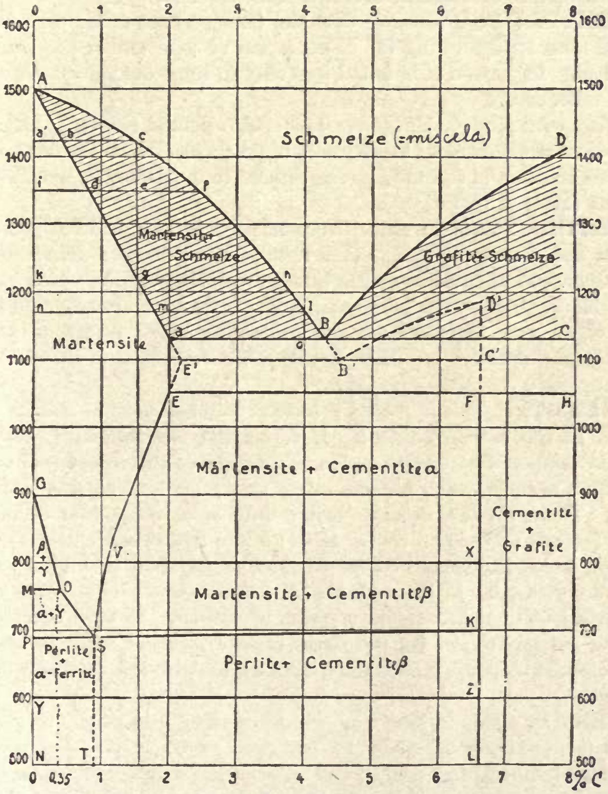


FIG. 327.

In the system *iron-carbon* there is separation of graphite independently of the presence of other substances, such as silicon, etc.; it is formed only if at least 2 per cent of carbon is present in the system and to a still greater extent if it approaches 4·3 per cent. The most favourable condition for the separation of graphite is the prolongation of the interval of solidification at 1130°. Silicon facilitates the formation of graphite by prolonging the duration of this eutectic point; manganese, on the other hand, abbreviates it.

The rest of the diagram is explained only by the considerations which follow.

(1) **FERRITE.** Under this denomination pure iron free from carbon (*a* iron) is under

stood. This product does not exist commercially, but is found, for example, in hypoeutectic steels, that is, steels which contain less than 0·85 per cent. of carbon (irons containing nickel, silicon, and vanadium in solution are also incorrectly called *ferrites*). Ferrite appears under the microscope in the form of polygonal faces produced from cubical crystals, by treating with tincture of iodine or, better still, with picric acid in 5 per cent. alcoholic solution or sodium picrate (solution in boiling water of 25 per cent. of sodium hydroxide and 2 per cent. of picric acid) (Plate I, Fig. *a*). On treating an exceptionally soft steel with a solution of 4 per cent. of nitric acid in amyl alcohol, if polygons of ferrite with well-defined contours appear they are a sign that the steel is brittle.

(2) **GRAPHITE.** This is evident without further treatment in the form of large, irregular, black veins. It is found in grey cast-iron (Plate I, Fig. *b*), in which the cementite forms white spots and bands, the pearlite small black bands, and the graphite large black veins. It is also seen in certain silicon and vanadium steels.

(3) **CEMENTITE : Fe_2C** (or **Iron Carbide**) (and perhaps other carbides in addition). This is formed abundantly during the cementation of steel, and is the hardest component of annealed steel. In general it is found free only in hypereutectic steels containing more than 0·85 per cent. of C.

On treatment with picric acid, cementite is not coloured (Plate I, Fig. *c*., where there are white bands of cementite and black plates of pearlite). If, on the contrary, it is treated with an alkaline solution of sodium picrate, cementite acquires an appearance of brownish-black striations (Plate I, Fig. *d*).

(4) **PEARLITE.** This is the eutectic product (pp. 257, 516 and 517) resulting from an alloy of ferrite and cementite, and is thus formed as superposed alternate laminæ of the one and the other. Picric acid or iodine tincture colours pearlite, which is, however, only very slightly coloured by sodium picrate. In Fig. *c* we have already seen pearlite, and in Plate I, Fig. *e*, we see a *hypoeutectic steel* containing black layers of pearlite and the remainder of bright ferrite. In Plate I, Fig. *f*, we see a *eutectic steel* with homogeneous layers and completely composed of pearlite.

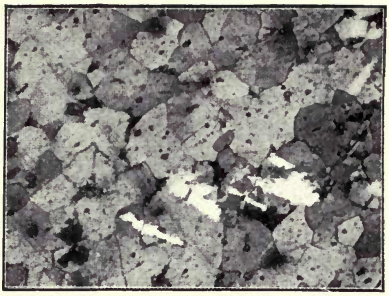
(5) **MARTENSITE.** This is a solid solution of carbon in iron, and its properties vary with variation of the carbon content. It forms the characteristic constituent of steel which has been tempered at temperatures a little above the transformation point. It is formed of minute needles which become larger as the eutectic steel is tempered at higher temperatures. These needles become visible only after the action of picric acid for 5 minutes (in 5 seconds there is no colour at all; dilute hydrochloric acid colours martensite a bright brown, whilst it does not colour *austenite*). In Plate II, Fig. *g*, the black needles of martensite are evident. In Plate II, Fig. *h*, we see martensite as much enlarged colourless needles in a hardened tool steel very rich in carbon. In such cases picric acid does not colour the martensite, whilst the dark, almost formless mass consists of *austenite*, which is not coloured by picric acid in the case of a steel with less carbon, whilst the martensite is coloured.

(6) **AUSTENITE.** This is found as a characteristic constituent of very highly carburised steels (containing more than 1·1 per cent. of C) which have been reheated for tempering to high temperatures (1000°) and immersed in a very cold tempering bath (below 0°). Austenite forms at the most 70 per cent. of the whole mass in a steel containing 1·65 per cent. of carbon. These steels ordinarily consist of a mixture of austenite and martensite, or rather of a mixture of austenite, troostite, and sorbite. The austenite forms almost shapeless masses which are comparatively soft; it is scratched by a needle, and except in special cases (*see above*, 5, Plate II, Fig. *h*) is not coloured by picric acid. In order to obtain a good hardened steel containing much austenite, steel containing 1·8 to 2·2 per cent. of carbon is heated almost to its melting-point and then immersed in mercury at 130°. According to Kurbatow (1909) austenite is probably an iron carbide of composition intermediate between Fe_6C and $Fe_{10}C$.

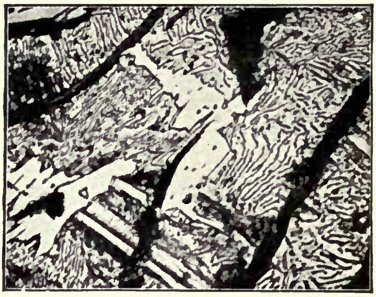
(7) **TROOSTITE** is the most important constituent of a steel tempered in water during the critical interval, or of a steel tempered at a higher temperature if an oil-bath is used for tempering, this being less active than water. It is coloured by picric acid even in 5 seconds, forming a black shapeless mass, thus differing from martensite (*see above*). Under the same conditions or after a few seconds' longer exposure, troostite forms grey needles, whilst austenite remains white (Plate II, Fig. *i*). It also acquires a dark colour under the action of nitric acid dissolved in amyl alcohol after 7 to 15 minutes.

(8) **SORBITE.** This is a product intermediate between troostite and pearlite. It may

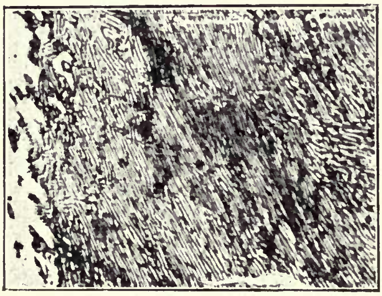
PLATE I



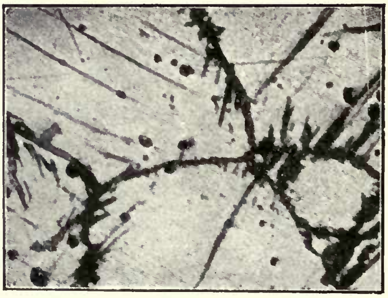
(*a*) Ordinary wrought-iron; light-coloured polyhedra of *ferrite* predominate; traces of *pearlite* (black spots) and small round black patches of slag. Magnification, 300 diams. Treated with picric acid.



(*b*) Grey cast-iron; *cementite* (white portion); *pearlite* (predominant laminated mass); *graphite* (black veins). Magnification, 500 diams.

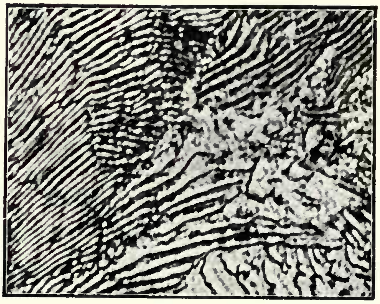


(*c*) Hypereutectic steel; *cementite* (white striations) surrounded by laminated *pearlite*. Magnification, 500 diams. Treated with picric acid.

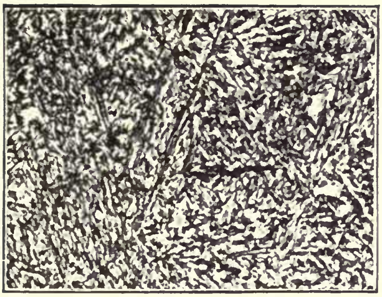


(*d*) Hypereutectic steel; *cementite* (black striations). Magnification, 500 diams.

(*e*) Hypoeutectic steel; *pearlite* in black laminæ, *ferrite*, light coloured. Magnification, 750 diams.



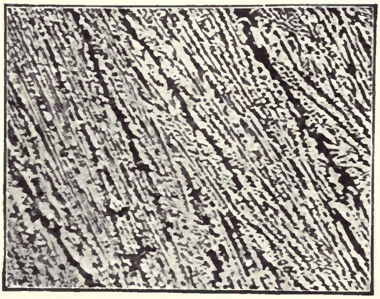
(*f*) Eutectic steel; lamellar *pearlite*.



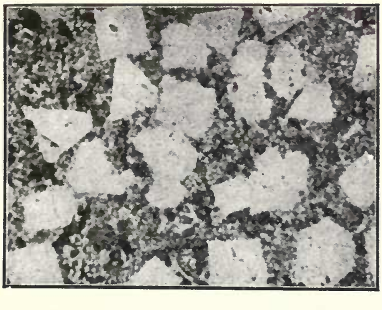
(*g*) Quickly quenched tool steel; *martensite* (dark needles). Magnification, 200 diams.

(*h*) Highly tempered tool steel, rich in carbon; *martensite* (white needles); *austenite* (dark, almost formless mass).

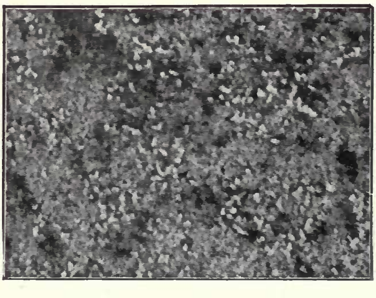
(*i*) *Troostite* (black); *martensite* (grey needles); *austenite* (white mass). Treated with picric acid for five minutes.



(*l*) White cast-iron; *cementite* (bright); *sorbite* (dark). Magnification, 500 diams. Treated with picric acid.



(*m*) Anti-friction metal (Pb, Sn, and Sb) for heavy loads. Magnification, 50 diams.



(*n*) Anti-friction metal for light loads. Magnification, 50 diams. Treated with hydrochloric acid.

be formed from martensite or on tempering steely cast-iron. It is easily coloured by picric acid, and in Plate II, Fig. *l* (500 diameters), it is shown together with colourless cementite in a *white cast-iron.* According to Kurbatow (1909) sorbite and troostite are solutions of carbon in α- and β-iron.

(9) **TROOSTO-SORBITE** is very similar to troostite.

In 1905 Le Chatelier classified the components of oridnary steels by considering them strictly as solid solutions, following the phase-rule :

(1) **The homogeneous constituents** which are the true phases. These are ferrite, graphite, and cementite. In special steels the ferrite may hold nickel, vanadium, etc., in solution, whilst the cementite may contain other carbides, such as Mn_3C, Cr_2C_3, etc.

(2) **Constituents consisting of eutectic aggregates :** Ferrite-cementite, which is simply pearlite.

(3) **Structural constituents,** such as martensite, austenite, troostite, troosto-sorbite, and sorbite. These products are stable more especially at high temperatures, and are formed from the so-called γ-iron at above 900°. By rapid cooling they are in great part dissociated. In general, pearlite changes into troostite by way of sorbite.

From these metallographic studies, extremely important practical conclusions may be derived. When pearlite and ferrite are found, one can affirm with certainty that the steel contains less than 0·85 per cent. of carbon and with experience one may estimate the carbon content within 0·1 per cent. Thus also, from the thickness of the ferrite, one may determine whether a steel is very soft, and if the ferrite polyhedra have clear contours, one may be certain that the steel is brittle. Further, a steel in which pearlite is present in parallel plates and bands is certainly brittle. A steel which has been heated to 900° and then slowly cooled is called a *normal steel.*

STATISTICS. *See* Footnote.[1]

---

[1] WORLD'S PRODUCTION OF IRON ORE, CAST-IRON, AND STEEL (IN THOUSANDS OF TONS)

	1880				1901				1906				1908			
	Cast-iron	Percentage of world's production	Steel	Percentage of world's production	Cast-iron	Percentage of world's production	Steel	Percentage of world's production	Cast-iron	Percentage of world's production	Steel	Percentage of world's production	Cast-iron	Percentage of world's production	Steel	Percentage of world's production
England . .	7,875	42·5	1,300	32·8	7,886	19·3	5,800	16	—	—	—	—	9,037	15	5,380	12
Germany . .	2,792	14·8	650	16·3	7,880	19·2	6,394	20	—	—	—	—	11,805	20	11,186	27
France .. .	1,725	9·4	360	9	2,400	5·8	1,465	4·7	3,200	6	2,500	7	3,412	5·8	2,713	6
United States .	3,879	21·2	1,000	25·2	16,132	39·5	13,690	44	25,300	49	24,000	64	26,000	43	26,700	65
Austria-Hungary	464	2·5	120	3	1,315	3·3	1,142	3·6	—	—	—	—	1,770	—	1,200	—
Russia . .	448	2·4	190	4·9	2,831	6·9	1,815	5·7	—	—	—	—	2,700	—	2,040	—
Belgium . .	608	3·2	110	2·9	765	1·9	526	1·8	—	—	—	—	1,380	—	2,150	—
Sweden . .	405	2·2	35	0·9	528	1·4	350	1·2	—	—	—	—	600	—	400	—
Italy . .	20	—	3	—	16	—	123	0·4	45	0·08	—	—	112	0·18	437	—
Spain . .	85	—	—	—	294	0·7	122	0·4	—	—	—	—	390	—	240	—
Other Countries	307	1·4	40	1·0	635	1·5	500	1·7	—	—	—	—	900	—	800	—
Total (approx.)	18,630	—	4,000	—	40,684	—	31,500	—	55,000	—	37,000	—	60,000	—	40,000	—

	1910		1912		1913		1914		1915		1916	
	Cast-iron	Steel	Cast-iron	Steel	Cast-iron	Steel	Cast-iron	Steel	Cast-iron	Steel	Cast-iron	Steel
England . . .	10,000	6,100	9,032	6,905	—	—	9,010	—	8,810	—	—	—
Germany . . .	14,800	13,700	17,900	17,302	19,310	—	14,390	14,950	11,790	13,190	—	—
France . . .	4,000	3,500	—	3,869	—	—	—	—	—	—	—	—
United States . .	27,600	26,500	29,200	31,752	30,700	27,500	22,700	21,000	30,396	—	40,118	42,000
Austria-Hungary .	2,056	—	1,750	2,785	—	—	—	—	—	—	—	—
Russia . . .	4,000	—	—	—	4,148	4,436	—	—	3,630	—	3,738	—
Belgium . . .	1,852	—	—	4,754	—	—	—	—	—	—	—	—
Sweden . . .	—	—	700	660	—	—	—	—	—	—	—	—
Italy . . .	—	—	—	—	—	—	—	—	—	—	—	—
Spain . . .	—	—	—	—	—	—	—	—	—	—	—	—
Other Countries .	—	—	—	—	—	—	—	—	—	387·3	—	333
Total (approx.) .	65,860	58,250	—	—	—	—	—	—	—	—	—	—

If the micrographic examination reveals the presence of pearlite and cementite, this is a sign that the steel contains more than 0·85 per cent. of carbon, and with increase of this amount the amount of cementite also increases. If the presence of martensite is observed and neither nickel, manganese, nor chromium is present, one may be certain that the steel has been tempered, and from the greater or lesser ease with which it is coloured one may deduce the carbon content; so from the greater or lesser size of the needles of martensite one may form an opinion as to whether the tempering has been carried out at the right temperature or at too high a temperature, or if ferrite is present together with the martensite, this is an indication that the steel is *hypoeutectic*, that is, that it has been tempered at too low a temperature. If, on the other hand, cementite is present together with martensite the steel is *hypereutectic*, and a shaft of cementation steel tempered in this manner, and more particularly when it shows free cementite in the form of needles, should be rejected on account of the brittleness of its surface layers. A special steel showing graphite is always brittle.

By means of the criteria with regard to which we have studied carbon steels micrographically, we may also study *special steels* containing nickel, chromium, manganese, silicon, tungsten,[1] aluminium, cobalt, titanium, etc., and we always obtain data of great

---

England imported 94,884 tons (£440,000) of cast-iron in 1909, and 138,460 in 1910, the exports having the value £2,760,000 in 1909, and £2,960,000 (1,206,000 tons) in 1910. Further, the imports of various iron and steel materials amounted to £9,080,000 in 1910, and £11,120,000 in 1911, and the exports to £42,960,000 in 1910, and to £43,760,000 in 1911.

Sweden exported 313,000 tons of different steels in 1908.

Spain produced 387,314 tons (£3,424,920) of iron and steel in 1915, and 322,931 (£4,803,740) in 1916.

Prior to 1879 *Germany* produced very little steel as its ores contain a certain amount of phosphorus and could be worked only after Thomas and Gilchrist's discovery; in 1909 20,000, and in 1911 60,000 tons of steel were produced in electric furnaces.

In 1912 the output of nearly 18,000,000 tons of cast-iron was furnished by 300 blast furnaces in which 33·5 million tons of iron ore, 622,000 of manganese ore, 17·2 millions of coke, and 3,328,000 of flux were used. In 1913 Germany exported 856,000 tons of cast-iron.

Of the iron produced in Germany in 1910, 25 per cent. was used for rails, sleepers, and rolling railway material, 45 per cent. for materials of construction (reinforcements for concrete, etc.), 15 per cent. for sheets and tinned sheets, and 10 per cent. for wire.

In *Italy* the Kjellin electric furnace was used in 1910 in the Lovère smelting works. The production in Italy is shown by the following figures (tons):

	Cast-iron	Wrought-iron	Steel	
			Crude	Finished
1903	90,744	195,521	187,361	154,134
1905	181,218	221,370	270,200	244,793
1907	149,000	265,757	430,000	346,749
1909	254,900	290,000	661,569	608,795
1911	342,586	305,223	736,000	697,958
1912	418,675	181,016	922,000	801,907
1913	458,806	144,820	933,500	846,085
1914	385,340	114,322	911,000	796,152
1915	377,510	70,510	1,009,200	854,470
1916	450,000	—	1,270,000	—

The exports of iron and steel from *Italy* are as follows: 2265 tons in 1914, 109,592 in 1915, and 15,634 in 1916. In 1915 Italy produced 3800 tons of cast-iron in electric furnaces, and in 1916 30,000 tons (£453,240). About 30,000 operatives were employed in the Italian iron industry in 1910.

Russia exported 179,630 tons of iron and steel in 1909, 237,000 workpeople being engaged in the iron industry in 1910.

In the *United States* in 1909, two Héroult electric furnaces taking 15 tons at each of 12 charges per 24 hours, produced 100,000 tons of steel. The enormous consumption of crude iron in America is higher than the output, so that importation is necessary, this amounting to 1,346,235 tons in 1916, and to 987,255 tons in 1917. In 1913 the production of 31,000,000 tons of iron is classified thus: 11,594,000 of Bessemer iron, 12,538,000 of basic iron, 340,000 of charcoal iron, 120,000 of ferromanganese, 111,000 of specular iron, 6,266,000 of ferrosilicon, etc.

Canada in 1913 produced 1,042,503 tons of steel (854,000 in 1912, 403,440 in 1911, 148,784 in 1910), 26·2 per cent. being Bessemer steel, 73·7 per cent. basic reverberatory steel, and 0·1 per cent. special electric steel.

In 1909 *China* produced 74,000 tons of crude iron.

[1] **Tungsten Steels.** These are rapid tool steels, which figured first at the Paris Exhibition of 1900, and were described by F. W. Taylor as the greatest triumph of the metallurgy of the alloys of recent times. Formerly cutting steels were hardened by a thermal process, tempering, based on the rate of transformation of the components of the system iron-carbon,

practical importance with respect to the limits of elasticity, the breaking load, brittleness, hardness, resistance to shock, etc. For instance, samples of steel for automobile gearing, made in America, contained 0·38 to 0·43 per cent. C, 0·82 to 1·05 per cent. Cr, 0·70 to 0·90 Mn, > 0·12 per cent. V.

The presence of 0·1 per cent. of Al suffices to prevent gas-bubbles in fused steel.

Although metallographic examination cannot entirely replace chemical analysis, yet in practice it is of great service on account of its rapidity (20 minutes sometimes suffices), which permits the different treatments to which the metal is exposed (hammering, rolling, heating, tempering, drawing, etc., etc.) to be followed closely. Thus, with iron treated in piles, the presence of inclusions of slag denotes the presence of much phosphorus. The presence of manganese is deduced from that of manganese sulphide, which is easily detected micrographically, whilst absence of manganese and a simultaneous high sulphur content are shown by the appearance of small pits on the polished surface. The relation of the dimensions of the peripheral and central granules of laminated iron indicate if the lamination was effected at the proper temperature, or if the block laminated for making wheels was too hot or had a nucleus still molten. Cast-iron rollers should show a preponderance of pearlite with a little cementite; otherwise they have not the desired hardness and wear easily when used.

The applications of micrography to the common metallic alloys are not less important. To what has already been stated on p. 517 *et seq.* concerning anti-friction metal (Sb, Sn, Pb) we may add that in alloys of lead, tin, and antimony, bright, hard, cubic crystals of SbSn, when they are very large, as in Plate II, Fig. *m*, and surrounded by the more plastic eutectic mixture, are suitable for bearings for heavy loads, and that these may be the greater the larger the surface occupied by these crystals; on the other hand, in Plate II, Fig. *n*, we see an anti-friction metal in which the crystals, SbSn, have almost disappeared and are extremely small, and this alloy is suitable for bearings for high speeds but light load. The micrographs were etched with hydrochloric acid.

---

which may have two micro-structures, the soft pearlite and the hard martensite structures. These two are reciprocally convertible. Thus, when heated for some time at above 786°, a soft steel is changed into the hard structure (endothermic process); while by slow cooling the latter becomes soft again (exothermic process); on the other hand, sudden cooling to below 200° by immersion in water or other substance does not give time for the conversion of the martensite into pearlite, and the steel remains hard, *i. e.*, tempered. Regulation of the cooling yields intermediate, less brittle steels, that is, the zone in the neighbourhood of the eutectic point is more or less extended. When tempered cutting tools are used they undergo heating and subsequent cooling, so that part of the martensite may be transformed into pearlite (loss of temper). To prevent this inconvenience an addition is made to the steel of tungsten, which forms a hard carbide stable at the most diverse temperatures. The maximum stable hardening is, however, obtained when, besides the tungsten (13 to 20 per cent.), some other metal is added, preferably chromium (2·5 to 5 per cent.); if such steel is heated to a high temperature (better 1200° than 1000°), the resistance of the temper becomes six or even eight times as great as that of an ordinary crucible steel. The life of cutting tools is hence greatly increased by the use of such steels. In 1910 3000 tons of tungsten were used to prepare 25,000 tons of special hard steels of the greatest value (8*s.* to £2 per kilo).

Tungsten increases the solidity or the breaking load and the elasticity and slightly diminishes the tenacity. Each 1 per cent. of tungsten produces an increase of about 6 kilos in the breaking load compared with that of ordinary steel, the maximum effect being exhibited by steels laminated and heated for tempering and by those poor in carbon.

Silicon Steel. This has the good qualities of steel poor in carbon (expansion, contraction, etc.), and of carbon-rich steel (high tensile strength). It is of growing importance in naval construction. Its strength being about one-third greater than that of ordinary steels of medium hardness, the amount of material may be reduced by about 25 per cent., and although its price is £4 more per ton, the practical advantages are pronounced. It was largely used in the construction of the *Mauretania* and *Lusitania*, and in France it is employed in making railway wagon tyres.

In making cylinders for compressed or liquefied gases use was made, in a particular case, of steels of the following compositions:

	Si Per cent.	S Per cent.	P Per cent.	Mn Per cent.	C Per cent.	Ni Per cent.	Cr Per cent.	V Per cent.
Soft steel .	0·192	0·016	0·015	0·50	0·23	—	—	—
Silicon steel .	0·980	0·026	0·035	0·95	0·39	—	—	—
Ni-Cr-V-steel.	—	0·017	0·012	0·32	0·32	3·3	1·6	0·19
Cr-V-steel .	0·031	—	0·049	0·60	0·20	—	1·05	0·15

These steels, especially the last, gave good results in all the strength tests of the cylinders. It would be possible to use steels even richer in silicon, provided that the carbon were kept within the limits 0·20–0·24 per cent., since the silicon steel tested was too rich in carbon (0·39 per cent.).

STATISTICS. The past century has been called the iron age on account of the large consumption of this metal for all purposes, especially for mechanical structures. Certain figures will best indicate the importance of this metal and will indicate how the increase in production of iron and steel may be considered as an index of the industrial progress of the individual nations.[1]

Everywhere, however, the production of soft iron is falling and that of steel rising rapidly; thus, in 1889, the world's output of soft iron was about 8,850,000 tons, whilst in 1901 it was only 4,600,000.

This is happening also in *Italy,* which, owing to its continued industrial development and its poverty in iron ore and its very great poverty in coal, has become a large importer of iron.[2]

In view of the extraordinary consumption of iron it does not seem out of place to consider whether there is any danger of exhaustion of iron ore, but our descendants of the twentieth century may still sleep quietly, as a shortage of iron is an eventuality which might perhaps interest the generations of the twenty-first century. Indeed, following deliberations of a conference held at the Hague in 1909 on the initiative of President Roosevelt, the results of such an investigation were presented to the XIth. International Congress of Geology, which met at Stockholm in 1910. It was shown that in the whole world there is a certain reserve of 22,400 million tons of iron ore, other probable deposits amounting to 129,377 million tons, and those at present utilisable to 10,200 million tons.

---

[1] In the past England almost held a monopoly in the iron and steel industry, but for several years the lead was taken by Germany; to-day, however, the United States outstrips all other countries. The iron industry is centred in enormous works of which we may mention those of Creusot in France, with 15,000 workmen, of Cockerill at Seraing in Belgium, with 12,000 workmen, the Krupp works in Germany, which at Essen alone employ 46,000 workmen, with a share capital of £9,000,000, and which showed a net profit in 1906–1907 of £1,200,000, and the works of the Carnegie Steel Company, the first American steel trust, which had a capital of £66,000,000, and produced 3,250,000 tons of steel in 1900, showing a profit of £4,800,000. During the European War all these works have greatly increased in importance, their output being trebled for war purposes.

The United States is at the head, not only with regard to production, but also with regard to the technical perfection of its processes, in spite of the great discoveries in this field of human activity which were made by the Englishmen, Cart, Bessemer, Siemens, Mushet, Thomas, Gilchrist, Lowthian-Bell, etc.

A workman in a steel works formerly earned 7½*d.* per ton of the product, whilst to-day he earns ½*d.* per ton, his total earnings being 20 per cent. larger than formerly with a smaller amount of labour, on account of the large daily production of modern machinery. The mean production of an English blast furnace is 220 tons per 24 hours, whilst in the United States it is 600 tons, but the ore worked in England contains 45 to 48 per cent. of iron on the average, whilst that worked in the United States contains 60 to 65 per cent. If it were not for the enormous internal consumption of iron in America, which sometimes obliges its importation from Europe, American competition would be fatal to the European iron industry.

[2] The imports were as follows (tons):

	1909	1910	1911	1912	1913	1914	1915	1916	1917
Wrought-iron and steel in plates, bars and wire	151,859 at £ 1,152,777	98,352	100,921	106,305	93,785	98,638	74,601	160,719	440,441
Crude pig iron and steel ingots	52,547 ,, 294,260	28,643	19,175	12,712	7,287	17,416	64,033	25,982	42,894
Refined cast-iron and ingots	246,730 ,, 937,574	204,854	234,770	267,355	221,697	219,995	240,535	302,333	315,954
Cast-Fe (rough castings)	14,202 ,, 109,849	18,491	20,031	14,905	12,219	11,425	4,830	2,059	2,910
Cast-Fe (finished castings)	7,619 ,, 162,576	6.928	7,742	5,244	3,216	3,180	1,215	880	937
Crude ferrosilicon containing 15 to 75 per cent. Si	136 ,, 3,164	511	155	—	—	100	—	—	237
Iron and steel rails .	12,894 ,, 82,526	16,575	11,172	12,434	7,155	5,252	1,872	10,469	36,303
Iron and steel tubes .	13,351 ,, 212,896	13,895	14,868	12,532	11,259	9,788	6,442	6,452	7,927
Unfinished wrought- and cast-iron and steel articles	5,212 ,, 95,177	4,633	7,027	8,310	8,870	3,498	2,276	2,229	15,975
Steel and iron in sheets	13,523 ,, 319,164	14,716	18,724	22,588	21,141	16,211	15,410	19,148	33,203
Tinplate and tinned, copper-plated, or oxidised iron and steel	1,390 ,, 30,977	1,350	1,626	1,032	1,198	751	709	548	750
Steel in springs . .	416,353 ,, 1,498,873	386,604	392,703	343,728	326,136	254,892	261,468	342,706	226,957
Wrought- and cast-iron and steel scrap	34,783 ,, 305,507	38,604	37,020	40,785	36,304	24,208	22,232	24,738	52.376

Of the last, 4733 million tons are in Europe, 5134 million in America, 156 million in Asia, 75 million in Africa, and 74 million in Australia. Of the ascertained reserves, 12,032 million tons are in Europe, 9885 million in America, 260 million in Asia, 136 million in Australia, and 125 million in Africa. Of the probable deposits, 86,822 million tons are in America, 41,029 million in Europe, 1000 million in Africa, 457 million in Asia, and 69 million in Australia.[1]

[1] Production and natural reserves of iron ore throughout the world (in millions of tons):

Country	Reserve			Production							
	Ascertained	Probable	Now utilisable	1905	1907	1910	1911	1912	1913	1914	1915
United States	10,000	—	—	—	52·5	54·2	45	55	58	—	—
Canada	—	—	—	—	—	—	—	—	—	—	—
Germany	3,607	—	1270	23·5 (with Luxemburg)	27·7	28·5	30	33·5	36	—	—
France	3,300	—	1140	—	8	—	—	—	—	—	—
England	1,300	37,700	455	—	16	15	15·3	14	—	—	—
Sweden	1,158	178	784	—	5	5·5	6·1	6·7	8·5	—	—
Russia	864	1,056	387	—	—	—	—	8·2	—	—	5·6
Spain	711	—	349	—	10	—	—	—	—	—	—
Norway	367	1,545	124	—	0·14	—	—	—	—	—	—
Luxemburg	270	—	90	— (*see* above)	—	—	—	—	—	—	—
Austria	250	323	90	—	2·5	—	2·8	5	—	—	—
Greece	100	—	45	—	—	—	—	—	—	—	—
Belgium	62	—	25	—	0·24	—	—	—	—	—	—
Hungary	33	78	13	—	—	—	—	—	—	—	—
Italy	6	2	3	0·37	0·52	—	—	—	—	—	—
Switzerland	1	2	—	—	—	—	—	—	—	—	—

The output of iron ore in the *United States* comes mostly from Minnesota.

England imported 8,000,000 tons (£6,280,000) of iron ore and scrap in 1910, while the imports in 1911 were valued at £5,800,000, and the exports in 1910 and 1911 at £480,000 and £460,000 respectively. The British output in 1912 was 14,000,000 tons: N. Riding of Yorkshire (Cleveland), 5,241,000; Northamptonshire, 2,568,285; Lincolnshire, 2,057,534; Cumberland and Lancashire, 1,593,522; Staffordshire, 809,598; Scotland, 579,100; Ireland, 61,364; other districts, 1,100,000 tons.

Algeria produced 970,000 tons of iron ore in 1907, 900,000 in 1908; the reserves are calculated to be more than 85,000,000 tons.

Tunisia in 1909 had a production of about 400,000 tons, the reserves being estimated at 40,000,000 tons.

In *Germany* the output of iron ore in different districts in 1908 was as follows (thousands of tons): Alsace and Lorraine, 13,282; Luxemburg, 5800; Prussia, 4312; Hesse, 304; Bavaria, 280; Brunswick, 128; Sachsen-Meiningen, 92; Waldeck, 20. In 1912 Germany used 44,000,000 tons of iron ore, of which 12,000,000 were imported (especially from Sweden, Spain, France); in 1911, 10,820,500 tons were imported, and in 1913 14,000,000 tons.

In *France* iron ore is obtained especially in the departments of Meurthe et Moselle and Meuse. In 1906 the output was 8,500,000 tons and in 1907 10,000,000 (418,000 of haematite), the exports (to Belgium and Germany) being 2,147,000 tons. The exports were 10,066,628 tons in 1913, 4,828,592 in 1914, and 94,864 in 1915, and the imports, 1,410,400 tons in 1913, 701,486 in 1914, and 271,160 in 1915. Most of the exported ore is from the rich deposits of Briey.

Italy is poor in iron ore, the richest mines being those of Elba, which give specular iron ore, haematite, magnetite, and limonite. Less important deposits are found in Sardinia, Brescia, Bergamasco, and Piedmont. Manganiferous iron ore is found at Monte Argentario near Port Ercole, and contains 40 per cent. Fe and 4 to 10 per cent. Mn. Prior to 1903 Italy exported about 143,000 tons of ore but afterwards much less, as is shown by the following figures (tons), which include manganiferous ore:

	1910	1911	1912	1913	1914	1915	1916	1917
Ore produced	577,000	380,268	582,066	603,116	706,246	679,970	946,604	—
,, imported	17,673	50,554	18,551	766	4,592	7,607	739	313
,, exported	9,892	22,851	12,313	9,700	8,943	157	30	326

In *Norway* about one-half of the ore is titanic magnetic ore (65 per cent. Fe, 10 to 15 per cent. Ti), which is worked with great difficulty in blast furnaces owing to its high melting-point (R. Pictet recommended the use of oxygen with such ores in the blast furnace. Treatment with CO at a relatively low temperature has also been suggested: *see* Norwegian Pat. 20,092, 1909).

Sweden exported 3,230,000 tons of ore in 1909, and 6,354,000 in 1913.

Spain had a production of 5,618,000 tons of iron ore (£1,424,000) in 1915, and 5,857,000 tons (£2,143,600) in 1916.

The price of crude cast-iron has only varied slightly, except during exceptional periods of short duration. In 1850 the price in England was about £2 5*s*., in 1880 £2 8*s*., and in 1902 £2 5*s*. per ton. The price rose exceptionally to £4 in 1854, £6 in 1873, and £3 12*s*. in 1900, while during the European War it increased in Italy to £24 or more. Nickel steel for armour-plating costs £120 per ton. The price of sheet iron and girders, formerly £8 per ton, rose enormously during the European War, and in 1917 girders were sold at £140 and sheets at more than £180 per ton. In Italy ordinary bar iron cost £64 per ton in 1916.

FERROUS COMPOUNDS

Iron forms two important classes of compounds. In the *ferrous* compounds the cation $Fe^{\cdot\cdot}$ is divalent, whilst in the *ferric* compounds the cation $Fe^{\cdot\cdot\cdot}$ is trivalent. Compounds of the former class have generally a greenish colour, whilst those of the latter class are brownish yellow.

Ferrous compounds are obtained on treating iron with acids with exclusion of the air, and also by reducing ferric compounds.

FERROUS OXIDE : FeO. This is obtained by the action of carbon monoxide on ferric oxide, $Fe_2O_3 + CO = CO_2 + 2FeO$; it forms a blackish powder which is easily oxidised on heating in the air. It melts at 1419°.

FERROUS HYDROXIDE : $Fe(OH)_2$. This is obtained as a greenish gelatinous mass by treating the solution of a ferrous salt with an alkali. It rapidly acquires a brown colour in the air as it is oxidised with formation of ferric hydroxide. It possesses feebly basic properties.

FERROUS CHLORIDE : $FeCl_2$. This compound is formed by the action of hydrochloric acid on an excess of iron and crystallises from the intensely green solution in green monoclinic prisms containing $4H_2O$. When prepared in the anhydrous state by the action of HCl vapour on hot iron it is white and the density of its vapours at 1400° corresponds with the formula $FeCl_2$. It readily forms well-crystallised double salts such as

$$FeCl_2, 2KCl, 2H_2O.$$

FERROUS SULPHATE : $FeSO_4$. This compound is found more or less pure in nature as the mineral *melanterite*, which occurs at Bilin (Bohemia), Goslar, Fahlun, Schemnitz, Bodenmais, Häzing (Tyrol), Guayaquil, etc. It crystallises in large, green, monoclinic prisms with $7H_2O$, and is then called *green vitriol* or *iron vitriol*. It is obtained by dissolving iron in dilute H_2SO_4, or preferably by partially roasting iron pyrites, FeS_2, and so transforming it into FeS, and then exposing the product to the action of moist air, which transforms it into $FeSO_4$ and H_2SO_4. The resulting ferrous sulphate is extracted with water and the solution poured into wooden vats containing iron turnings in order to neutralise the small amount of free H_2SO_4 and to reduce to ferrous sulphate the small amount of ferric sulphate which is mixed with the mass. The solution is then evaporated in presence of iron, decanted from the yellow sediment which is thus formed, consisting of basic ferric sulphate and gypsum, and the green vitriol is then allowed to crystallise. The firm of Schnorf Bros. at Uetikon work up burnt pyrites to a paste with hot sulphuric acid of 60° Bé. (as obtained in the Glover tower), and after stirring, and when the reaction is finished, the product is dissolved in water and reduced to ferrous sulphate by the action of iron turnings. The solution is concentrated to 35° to 36° Bé. (measured at 90°), and is allowed to cool in the presence of hoop-iron which is suspended in the liquid. Ferrous sulphate is thus obtained in a more economical manner, and the disadvantage of the evolution of hydrogen which occurs on dissolving Fe in H_2SO_4 is avoided. Ferrous sulphate is isodimorphous with the sulphates of the magnesium series, and also forms well-crystallised stable double salts, such as Mohr's salt, $FeSO_4,(NH_4)_2SO_4,6H_2O$, which forms green crystals very stable in the air and is used in volumetric analysis.

At 100° ferrous sulphate loses $6H_2O$, whilst the last molecule of water is evolved at 300°. When exposed to moist air it becomes brown and is transformed into basic ferric sulphate:

$$3FeSO_4 + O + H_2O = Fe_2(SO_4)_3, Fe(OH)_2.$$

100 parts of water at 10° dissolve 61 parts of crystallised ferrous sulphate, at 25° 115 parts, and at 100° about 333 parts. The green solution absorbs much nitric oxide, turning brown.[1]

It is used technically in large quantities for mordanting wool which is to be dyed with logwood black. It is also used as an economical disinfectant and absorbs both H_2S and NH_3; also in the manufacture of black ink, Prussian blue, etc. It costs £2 to £2 16*s.* per ton, and when chemically pure £10 per ton.

France exported 1852 tons of ferrous sulphate in 1913, 1968 in 1914, and 550 in 1915. The *Italian* production and exportation were as follows (tons):

	1909	1910	1911	1912	1913	1914	1915	1916	1917
Production	2000	2263	1076	2139	1480	1392	1714	—	—
Exportation	97	65	51	57	87	42	55	164	350

FERROUS CARBONATE: $FeCO_3$. This compound is found naturally as *Siderite*, and also dissolved in mineral waters through the action of CO_2, in the form of **Ferrous bicarbonate**, $Fe(CO_3H)_2$, but separates from such water in the form of insoluble ferric hydroxide on contact with air. The basic carbonate is also formed on adding an alkali carbonate to a solution of a ferrous salt, but is very unstable, as the $Fe^{\cdot\cdot}$ ions, being weakly basic, do not yield stable salts with weak acids. It quickly becomes brown in the air, being transformed into $Fe(OH)_3$.

FERROUS PHOSPHATE: $Fe_3(PO_4)_2 + 8H_2O$. This occurs in nature as *Vivianite* in bluish crystals. It is obtained by the action of sodium phosphate on solutions of ferrous salts, as a white amorphous, easily oxidisable powder.

FERROUS SULPHIDE: FeS. On melting iron and sulphur together or even on moistening a mixture of iron filings and flowers of sulphur in the air, a blackish mass of metallic lustre is obtained which consists mainly of FeS, and is used in the laboratory for the preparation of hydrogen sulphide by treating it with HCl or H_2SO_4. It is obtained pure as a black precipitate by treating a solution of a ferrous salt with an alkali sulphide, but FeS is readily oxidised in the air and transformed into ferric sulphate. Instead of starting from a ferrous salt a ferric salt may be used, as it is reduced by the alkali sulphide and then precipitated:

$$2FeCl_3 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S$$
$$FeCl_2 + (NH_4)_2S = 2NH_4Cl + FeS.$$

Italy produced 30 tons of ferrous sulphide in 1905, of the value of £480.

FERRIC COMPOUNDS

These have a brownish-yellow colour and are formed by the oxidation of ferrous salts. They may be easily reduced again to ferrous salts. They contain a trivalent ion, $Fe^{\cdot\cdot\cdot}$, which has weakly basic properties and cannot therefore

---

[1] This characteristic reaction of **ferrous salts** is reversible, NO and the ferrous salt being regenerated if the solution is either heated, or placed in a vacuum, or treated with a current of an inert gas; the absorption of NO is governed by the law of mass action. The compound formed always contains the divalent cation $[Fe(NO)]^{\cdot\cdot}$, and the brown substance is $[Fe(NO)]Cl_2$ or $[Fe(NO)]SO_4$, although these have not yet been isolated unchanged. The action of NO on $FeSO_4$ in sulphuric acid yields an intense red coloration, the compound being less dissociated than in aqueous solution (with HCl the colour is deep green): addition of water produces the characteristic brown coloration of the cation $[Fe(NO)]^{\cdot\cdot}$. The red compound is perhaps derived from ferrosulphuric acid, $FeSO_4, xH_2SO_4$, and the green from ferrohydrochloric acid, $FeCl_2, xHCl$. Similar nitroso-compounds are obtained from cupric salts in presence of acids, dilution then giving NO—from the cation $[Cu(NO)]^{\cdot\cdot}$. Osmium and ruthenium salts, etc., yield similar compounds. Nitric oxide is absorbed also by pentacyano-ferrous salts, *e. g.*, $[FeCy_5(NH_3)_3]Na$, in presence of acetic acid, to form ferrous nitroprussiate, $[FeCy_5(NO)]Na_3$, whilst ordinary ferric nitroprussiate has the formula, $[FeCy_5(NO)]Na_2$ (K. A. Hofmann, 1895; W. Manchot, 1912 and 1913; I. Bellucci, 1913).

form salts with weak acids, whilst the salts with strong acids are readily hydrolised in aqueous solution (*see* pp. 97, 108, 271).

FERRIC OXIDE : F_2O_3 (or **Iron Sesquioxide**). This is found in nature in compact reddish masses in the form of *hæmatite* or as *specular iron ore*, which is a crystalline anhydride, or as *ochre*, which is more or less highly coloured from yellow to red. It is obtained artificially as a bright red powder by heating ferric hydroxide or ferrous sulphate to redness in the air. It is then called *iron red, English red, caput mortuum* or *colcothar.*

It melts at 1548°, and is stable up to 1600°, when it loses a little oxygen; it evaporates freely at 1800° and completely at 2000°.

It is abundant in a very impure condition as burnt pyrites (pp. 291, 324).

It is used as a red pigment in paints, and for polishing glass. Its price varies according to its degree of fineness from £6 to £10 per ton.

It is now obtained in various brightly coloured qualities of different shades by heating ordinary iron oxide mixed with 6 per cent. of sodium chloride to redness for several hours in clay crucibles, and then allowing it to cool slowly out of contact with the air. By varying the temperature and the duration of the heating, various shades are obtained from a bright red to a reddish violet.

Of late years various patents have been taken out for the preparation of such iron pigments (Ger. Pat. 143,517, Eng. Pat. 16,338 of 1903, and U.S. Pats. 739,444 and 758,687).

The production and importation of ferric oxide (English red) into *Italy* are as follows (tons), the exports including burnt pyrites (*see* Footnote, pp. 291, 292):

	1905	1908	1909	1910	1912
Production . .	750	1630	—	—	—
Importation . .	596	1140	1045	1,487	1,749
Exportation . .	—	6000	9691	14,330	46,133

France in 1913 exported 184 tons of ferric oxide, in 1914 273 and in 1915 188 tons. The exports were 36,937 tons of ground ochre in 1913, 32,580 in 1914, and 15,142 in 1915.

England produced 16,313 tons of ochre in 1909 and 16,515 (£15,400) in 1910.

The imports of mineral pigments, both natural and artificial, were 964 tons in 1906 and 982 tons in 1908, of the value of £4680, apart from 1643 tons of umber, of the value of £2288. The exports were 3300 tons in 1908, of the value of £13,280. *Germany* exported 3910 tons of mineral pigments in 1905.

FERRIC HYDROXIDE : $Fe(OH)_3$. This is formed as *rust* on iron exposed to moist air, or as a voluminous reddish-brown precipitate on treating a solution of a ferric salt with an alkali. It is best to use NH_3, as the precipitate is then more easily washed. It is insoluble in water and soluble in acids. When freshly precipitated it is soluble in a solution of ferric chloride or acetate, and by dialysing this solution a pure reddish-brown colloidal solution of $Fe(OH)_3$ is obtained which is used in medicine. On boiling the hydroxide for some time with water, it is transformed into $Fe_2O(OH)_4$, that is, into a hydroxide which is partially soluble in acids, and which is also found naturally as *limonite.*

Ferric hydroxide is a weak base.

FERROSO-FERRIC OXIDE : Fe_3O_4. This is found naturally as *magnetite* or *magnetic iron ore*, which abounds in Sweden, Norway, and the Ural Mountains. It is formed on burning iron in excess of oxygen or on heating iron in a current of steam or of CO_2. It is sometimes used as a pigment. It melts at 1538°.

FERRIC CHLORIDE : $FeCl_3$. This compound is obtained on passing a current of chlorine into a solution of ferrous chloride, or by oxidising such a solution with HNO_3. It crystallises with various amounts of water (from 5 to 15 mols.), but when heated it loses not only water, but also HCl (similarly to $MgCl_2$); anhydrous $FeCl_3$ is only obtained by heating iron in a current of dry chlorine. It is soluble in water, alcohol, and ether. The density of its vapour at 400° corresponds with the formula Fe_2Cl_6, whilst at 1000° it corresponds with $FeCl_3$.

Its molecular weight has been determined by the rise of the boiling-point of an ethereal solution.

It is used in the chlorination of copper and silver and as a mordant in dyeing textile fabrics. It is also used for purifying effluent waters. In solution of 40° Bé. it costs about £14 8*s.* per ton. The solid crystalline salt costs £20 per ton.

FERRIC SULPHATE : $Fe_2(SO_4)_3$. This compound is obtained on dissolving ferric oxide in sulphuric acid or by oxidising ferrous sulphate with HNO_3. On evaporation a whitish substance remains which dissolves in water with a brownish-red colour. It is the principal component of *ferrugine* used in dyeing silk and cotton (*see* Vol. II., "Organic Chemistry"). With the alkali sulphates it forms well-crystallised alums such as K_2SO_4, $Fe_2(SO_4)_3$, $24H_2O$.

Italy produced 149 tons of ferrugine in 1914 and 69 tons (£400) in 1915.

FERRIC PHOSPHATE: $FePO_4$. This is a yellowish powder, insoluble in water and acetic acid, which is obtained by precipitating a solution of a ferric salt with sodium phosphate.

FERRIC SULPHIDE : FeS_2. This forms *iron pyrites*, which is found abundantly in nature in lustrous, hexahedral, pentadodecahedral and often octahedral golden-yellow crystals. It is used for the manufacture of sulphuric acid (*see* p. 291).[1]

Its density is 5·5 and its hardness 6 to 6·5; when struck with a steel it sparks When it is heated on charcoal in the blowpipe flame, the sulphur burns away and there remains black oxide of iron, which is attracted by a magnet. When it is heated in a test-tube sulphur (sometimes coloured brown by arsenic) sublimes. It resists the action of hydrochloric acid, but nitric acid attacks it with separation of sulphur.

In nature it occurs more rarely as *marcassite*, in pale yellow to greenish, trimetric crystals, and as *pyrrhotite* or *magnetic pyrites* in crystals of the hexagonal system (density 4·5, hardness 3·5 to 4·5); this contains only 36·4 per cent. S (i.e., FeS), is often accompanied by nickel and cobalt, and with HCl yields H_2S and sulphur.

POTASSIUM FERRATE : K_2FeO_4. This compound is formed on heating iron filings

---

[1] *Iron pyrites* abounds in various countries. *Italy*, which until recently imported large quantities, now exports pyrites. Its most important deposits are those of Valle d'Aosta (48 to 50 per cent. S and 1 per cent. As), Brosso, near Turin (less than 0·2 per cent. As), Libiola and Casarca in Liguria, and Torrebelvicino, Agordo and Rivamonte in Venetia. Since 1912 the mines of Montieri and Gavorrano in the province of Grosseto (46 to 48 per cent. S) have assumed great importance, and contribute most largely to the exports.

In *Germany* poor pyrites (32 to 42 per cent. S) occurs sparsely in Westphalia (at Meggen and Schwelen). In *Hungary* it is found at Schwellnitz (46 to 47 per cent. S). In *France* at Saint-Bel and Chessy (Rhone), in Gard and Ardeche (Soyons) (45 to 48 per cent. S). In *Norway* at Ytterven and Trondhjem (38 to 44 per cent. S). In *Sweden* at Fahlun, together with copper ore. In *England* in small amounts in Cornwall, Devonshire, and Yorkshire (24 to 34 per cent. S). In *Belgium* at Namur (34 to 42 per cent. S). In the *United States* in the states of New York, Massachusetts, Virginia, Georgia, etc. (38 to 48 per cent. S). The countries with the largest deposits of pyrites are *Portugal* (S. Domingo) and especially *Spain*, at Tharsis, Rio Tinto, Burton, Poderosa, etc. (46 to 50 per cent. S).

The *world's output* has been given on p. 292.

Spain produced 911,624 tons of copper pyrites and 2,113,521 of iron pyrites in 1912, in which year 130,182 tons of copper pyrites were exported to Germany, 194,700 to England, 249,615 to Holland, and 268,768 to the United States. Of the iron pyrites, Spain exported 353,204 tons to Germany, 344,100 to France, 336,600 to England, 263,380 to Holland, and 536,100 to the United States. About two-thirds of the Spanish output comes from Rio Tinto. In 1915 Spain produced 730,000 tons of iron pyrites and 1,464,350 of copper pyrites, the production in 1916 being 953,678 and 1,748,742 tons respectively.

The *United States* imported 1,264,493 tons of pyrites in 1916 and 928,864 in 1917.

France produced 270,000 tons of pyrites in 1913 and imported 581,756 tons in 1913, 604,656 in 1914, 421,986 in 1915, and 792,347 in 1916.

England produced 11,427 tons of pyrites in 1913 and 11,654 (£4760) in 1914.

Germany is normally a large importer of pyrites. During the European War, much sulphuric acid was prepared from gypsum (*see* p. 307), and, as most of the sulphuric acid used in making explosives is recoverable in a diluted state, large concentration plants were organised. In 1915 400,000 tons of pyrites were imported from Norway.

Sweden produced 16,100 tons of pyrites in 1909.

Norway exported pyrites to the value of £220,000 in 1909 and 390,000 tons in 1913; in 1915 400,000 tons were exported to Germany. Norway consumes annually about 40,000 tons of pyrites.

Holland imported 351,277 tons of pyrites in 1909.

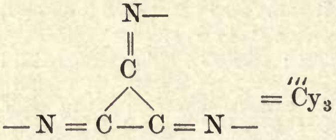
The statistics for *Italy* are (tons):

	1914	1915	1916	1917
Production .	335,531	369,300	410,300	about 450,000
Importation .	27,254	24,165	2	—
Exportation .	73,880	47,740	145,786	170,302

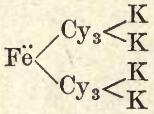
with saltpetre or by suspending ferric hydroxide in an alkaline solution through which a current of chlorine is passed. It forms dark red crystals, isomorphous with potassium sulphate and chromate. It is decomposed by water with evolution of oxygen and separation of $Fe(OH)_3$. This compound may be considered as the potassium salt of a hypothetical **Ferric Acid.**

CYANOGEN COMPOUNDS OF IRON

When nitrogenous organic matter is melted with iron and an alkali carbonate iron cyanides are formed. If potassium cyanide is added to the aqueous solution of a ferrous or ferric salt, yellow precipitates of ferrous cyanide, $Fe(CN)_2$, or ferric cyanide, $Fe(CN)_3$, are formed, which are decomposed by the air and dissolve in an excess of KCN, forming the double cyanides, $Fe(CN)_2$, 4KCN and $Fe(CN)_3$, 3KCN; these no longer show the ordinary reactions for iron with KOH, H_2S, etc., nor those of ordinary cyanides. It must, therefore, be assumed that they contain complex ions instead of the Fe ion, namely, the tetravalent ferrous anion, $FeCy_6''''$ (where Cy is an abbreviation for cyanogen, CN), which forms **ferrocyanides**, and the trivalent ferric anion, $FeCy_6'''$, which forms **ferricyanides**. On adding concentrated HCl to strong solutions of these salts, the corresponding acids, H_4FeCy_6 and H_3FeCy_6, separate as white powders which become blue in the air. If we imagine a trivalent radical formed of three cyanogen groups:

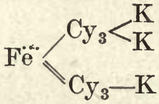


we may imagine potassium ferrocyanide and ferricyanide to be constituted as follows:



Potassium ferrocyanide

and



Potassium ferricyanide

POTASSIUM FERROCYANIDE: K_4FeCy_6 (Yellow Prussiate of Potash). This was once prepared almost exclusively by the addition of dry animal refuse, such as blood, hides, horns, leather cuttings, etc., and iron turnings to red-hot molten potassium carbonate. Ferrous sulphide was thus formed from the organic sulphur, together with KCN, and on lixiviation a solution of potassium ferrocyanide was formed without further treatment, the insoluble residue being used in place of animal charcoal as a decolorising agent, *e. g.*, for ozokerite, paraffin wax, etc.: $6KCN + FeS = K_4FeCy_6 + K_2S$. By concentrating and recrystallising, potassium ferrocyanide was obtained in large translucent monoclinic yellow prisms, containing $3H_2O$; these have a sweetish and then a bitter taste, are non-poisonous, and at 100° lose all their water of crystallisation, yielding a white powder soluble in 4 parts of cold or 2 parts of boiling water, and insoluble in alcohol. Nowadays the yellow prussiate is made almost exclusively from Laming mixture, which is formed in abundance in the purification of illuminating gas[1] and consists mostly of lime, oxide of

---

[1] The coal used in making lighting gas (*see* Vol. II., "Organic Chemistry") contains from 1·25 per cent. (Silesian) to 1·30 per cent. (Westphalia) to 1·45 per cent. (English) of nitrogen, of which 16 per cent. appears in the crude gas as ammonia and 4 per cent. as cyanogen compounds, the rest being lost; 1 cu. metre of gas contains 1 to 3 grms. of free and combined HCN. In modern gas-works the cyanogen compounds of the gas are partially fixed, according to the Bueb process (Ger. Pats. 112,459 of 1900 and 122,280), by absorption in concentrated ferrous sulphate solution (20° Bé., *i. e.*, 280 grms. of $FeSO_4,7H_2O$ per litre); this does not fix the ammonia, which is absorbed by water. For both absorptions, use is made of large iron cylinders known as *Standards* (*see* Vol. II., Illuminating Gas). The sulphur is then removed from the gas by oxide of iron in the ordinary way. The Bueb wet process completely removes the cyanogen compounds and is three times as efficient as the old method with oxide of iron. The yield of cyanogen

iron and sulphur (35 to 50 per cent.), together with ferrocyanides (10 to 15 per cent.) and thiocyanates (1 to 4 per cent.). The mass is first lixiviated with water to remove the thiocyanates,[1] ammonium sulphate (1 to 4 per cent.) and other soluble salts, and is then heated with powdered slaked lime by steam at 40° to 100° in closed vessels to recover the ammonia distilling over and to obtain calcium ferrocyanide in concentrated aqueous solution; the insoluble residue, which contains more than 40 per cent. of sulphur, is dried and used in pyrites burners for making sulphuric acid. Addition of KCl to the boiling calcium ferrocyanide solution results in the separation of the almost insoluble double salt of calcium and potassium ferrocyanide, $K_2CaFeCy_6$ (the calcium and sodium salt is highly soluble), and when this is heated with K_2CO_3 solution, potassium ferrocyanide solution (which crystallises after concentration to 32° to 35° Bé. in a vacuum) is obtained together with insoluble $CaCO_3$. If, however, it is heated with Na_2CO_3 (Na_2SO_4 not so good),

---

compounds may be reduced to one-half if the coal used has been long exposed to the weather. The cyanogen compounds are fixed by the Bueb process as a paste containing insoluble $(NH_4)_6Fe(FeCy_6)_2$ and soluble $(NH_4)_4FeCy_6$, in addition to 3 per cent. of ammonia as sulphate. The paste, containing about 13 per cent. of cyanides calculated as K_4FeCy_6, 6·44 per cent. NH_3, 5·5 per cent. of total Fe, and about 1·8 per cent. S, is heated by direct steam in closed boilers provided with stirrers, the ammonia distilling off being collected apart. The residual cyanogen compounds, all insoluble now, are collected in filter-presses and heated with milk of lime, any ammonia evolved being collected and the residue filter-pressed to obtain calcium ferrocyanide solution; to this KCl and K_2CO_3 are added, the potassium ferrocyanide being purified by slow crystallisation. If sodium ferrocyanide is required, the calcium ferrocyanide solution is treated with the calculated quantity of NaCl (Ger. Pat. 169,292, 1904) and evaporated to incipient separation of the double calcium and sodium salt, $CaNa_2FeCy_6$, which is only slightly soluble in the hot. Further concentration is effected in a vacuum at a comparatively low temperature, the salt then redissolving. From the highly concentrated solution thus obtained, crystals separate on cooling; these are removed, while the solution is concentrated further in a vacuum at 60° until the double salt again begins to deposit. The hot solution is then decanted off, and on cooling gives crystals of sodium ferrocyanide, the mother-liquor being afterwards heated to such temperature that all the double salt is precipitated. This is separated from the final mother-liquors (which contain $CaCl_2$), dissolved in hot water together with NaCl and the solution concentrated, the sodium ferrocyanide being then allowed to crystallise out.

Feld (Ger. Pat. 178,635, 1905) fixes the cyanogen compounds in the soluble state by using more dilute ferrous sulphate (20 per cent. of $FeSO_4$, $7H_2O$) in which the iron is precipitated beforehand as insoluble cyanogen compound. In this way the formation of FeS is avoided, while soluble cyanogen compounds (90 per cent.) are gradually formed.

Foulis (Eng. Pat. 15,168, 1895) and Rutten (1902), like Brunnquell (1856) and Knoblauch (1886) fix the cyanogen compounds with iron hydrocarbonate (obtained by treating a hot solution of 120 kilos of ferrous sulphate with a hot solution of 55 kilos of Na_2CO_3, and collecting the washed precipitate of $Fe(OH)_2,FeCO_3$ on a filter), which is mixed with 600 litres of water containing 60 kilos of K_2CO_3, and the mass introduced into the ordinary scrubber (Standard). The solution of K_4FeCy_6 formed is filtered, freed from ammonia in a Feldmann or other column (*see* p. 358), filtered again and concentrated in a vacuum to crystallisation. The sludge on the filters is heated with KOH to recover the ammonia, and then collected on a filter and again used to absorb the cyanogen compounds of lighting gas. Instead of K_2CO_3, Davis and Neill use Na_2CO_3, thus obtaining sodium ferrocyanide.

W. Feld (Ger. Pat. 141,624) proposes to fix the cyanides—after removal of CO_2 and H_2S from the gas—with suspensions of magnesium compounds, the magnesium cyanide thus formed being decomposed by boiling: $Mg(CN)_2 + 2H_2O = Mg(OH)_2 + 2HCN$.

[1] The thiocyanate is extracted as ammonium thiocyanate, $NH_4 \cdot CNS$, mixed with ammonium sulphate, and these two salts often separate by simple fractional crystallisation. If this cannot be effected, their solution is heated with milk of lime, the ammonia thus liberated being fixed by means of sulphuric acid, whilst the calcium thiocyanate solution is filtered off from the precipitated calcium sulphate and is then transformed either into ammonium thiocyanate with the calculated quantity of ammonium sulphate, or into white, insoluble copper thiocyanate, CuCNS, which is used for safety matches (*see* p. 408) and for dyeing with aniline black.

Ammonium thiocyanate is prepared industrially also by heating a mixture of carbon disulphide and ammonia under pressure at 100°; ammonium thiocarbonate is first formed and this is transformed at 105° into H_2S and ammonium thiocyanate in the form of colourless crystals, which are readily soluble in water or alcohol and redden in the air. It is used in printing textiles (as preservative) and in making artificial mustard oil. It costs about £80 per ton.

Potassium thiocyanate, KCNS, is obtained, according to Tscherniack and Günsburg, by treating ammonium thiocyanate with lime—the ammonia being recovered—and adding potassium sulphate to the calcium thiocyanate, this giving insoluble gypsum and a solution of potassium thiocyanate. Gélis, however, heats CS_2 with ammonium hydrosulphide and treats the ammonium thiocarbonate formed with potassium sulphide. Fusion of potassium ferrocyanide with sulphur, extraction with alcohol and evaporation of the solvent yields potassium thiocyanate in colourless, deliquescent, prismatic crystals, which redden in the air. It is used as a mordant in dyeing and printing textiles, in photography, and in making artificial mustard oil (for other thiocyanates, *see* Vol. II., " Organic Chemistry ").

sodium ferrocyanide is obtained, this being more soluble in water and crystallising from very concentrated solutions with $12H_2O$; it is obtained pure by repeated crystallisation. Sodium ferrocyanide is now obtained from the sludge obtained in purifying illuminating gas by the Bueb process (*see* Vol. II., " Organic Chemistry ").[1]

Potassium ferrocyanide dissolves in 4 parts of cold water or 2 parts of hot water. It is decomposed at a red heat into $KCN + FeC_2$ (iron carbide). It forms HCN on heating with dilute H_2SO_4, whilst with strong H_2SO_4 it forms CO according to the following equation :

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 3(NH_4)_2SO_4 + 2K_2SO_4 + FeSO_4 + 6CO.$$

If potassium ferrocyanide is added to the solution of a ferric salt, a blue coloration, and then an intensely blue precipitate, is formed which is *Prussian blue,* a ferric ferrocyanide :

$$3K_4FeCy_6 + 4FeCl_3 = 12KCl + Fe_4^{\cdots}(Fe''Cy_6)_3 :$$

this compound is insoluble in acids and is decomposed by alkalis :

$$(FeCy_6)_3Fe_4 + 12KOH = 4Fe(OH)_3 + 3FeCy_6K_4.$$

The formation of Prussian blue is a sensitive reaction for ferric salts.

With copper salts potassium ferrocyanide forms a bright red precipitate of cupric ferrocyanide, insoluble in acids and decomposed by alkalis :

$$K_4FeCy_6 + 2CuSO_4 = 2K_2SO_4 + Cu_2FeCy_6.$$

This reaction is extremely sensitive and serves for the detection of minimal traces of copper salts.

With *ferrous* salts potassium ferrocyanide forms a white precipitate which becomes blue in the air. **Potassium Thiocyanate, KCNS,** forms a blood-red coloration of ferric thiocyanate with ferric salts : $3KCNS + FeCl_3 = 3KCl + Fe(CNS)_3$.

USES AND STATISTICS. Potassium ferrocyanide is used (*see* Vol. II., " Organic Chemistry ") in silk dyeing, for making Prussian blue and for tempering iron, and is now scarcely ever employed for the manufacture of potassium cyanide (*see* p. 547). Sodium ferrocyanide may replace the potassium salt, but is never so pure. It costs £40 to £48 per ton. *Italy* produced 247 tons of calcium ferrocyanide (£2866) in 1908, 241 tons (at £10 8*s.* per ton) in 1913, 110 tons in 1914, and 261 tons (at £12 per ton) in 1915. Italy produced also 72 tons of sodium ferrocyanide (at £12 per ton) in 1915 and imported yellow (and a little red) prussiate to the extent of 286 tons in 1906, 233 in 1911, 127 in 1913, 54 in 1915, and 0·2 in 1917. *France* exported 583 tons of sodium and potassium ferrocyanides in 1913 and 275 in 1915.

The world's output of ferrocyanides in 1899 was about 11,000 tons : 4000 in Germany and Austria together, 3000 in England, 1500 in France, 1500 in the United States, and 500 in Holland and Belgium. The production in the United States has now increased, and in Germany reached about 4000 tons in 1913.

FERRIC FERROCYANIDE (Prussian Blue), $Fe^{\cdots}_4(FeCy_6)_3$, was discovered accidentally by Diesbach in 1704 at Berlin. It has since been used as a fine blue pigment very stable towards light and acids and very unstable towards alkali. Nowadays, however, it is employed but little, owing to the competition of aniline colours and ultramarine for painting and printing paper and carpets, dyeing silk (*see above*) and blueing laundry.

It is prepared industrially in various ways : by treating potassium ferrocyanide (or

---

[1] The crude illuminating gas, after being washed with water, is passed into a horizontal revolving washer containing ferrous hydroxide suspended in caustic soda solution. This fixes all the cyanogen compounds (about three times as much nitrogen is fixed as in the dry way with Laming mixture). When the liquid has assumed a pasty consistency, it contains mainly insoluble ammonium ferrosoferrocyanide, $Fe^{\cdot\cdot}(NH_4)_6(FeCy_6)_2$, with a little ammonium ferrocyanide, ferrous sulphide, ammonium sulphate and carbonate (altogether 15 to 20 per cent. of cyanogen calculated as sodium ferrocyanide). The paste is boiled to render the soluble cyanides insoluble by means of the FeS present, the ammonium carbonate being distilled off; the mass is then filtered, ammonium sulphate being obtained from the filtrate, while the residue is heated with slaked lime, the rest of the ammonia being thus recovered. The calcium ferrocyanide solution remaining is heated with sodium carbonate, this precipitating calcium carbonate and leaving in solution moderately pure sodium ferrocyanide, which crystallises out after concentration in a vacuum. In the Stockholm gas-works, 29 tons of sodium ferrocyanide were thus obtained in 1907, 53 tons in 1908, and 100 tons of the pure crystallised salt in 1910.

crude calcium ferrocyanide) solution with ferric oxide solution (obtained by oxidising ferrous sulphate with nitrosulphuric acid), or by mixing yellow prussiate and ferrous sulphate solutions and oxidising the whitish precipitate thus formed by means of chlorine or nitric acid. The decanted precipitate, washed, filtered and dried, forms a light indigo-blue mass with copper-red reflection, and is readily reducible to an impalpable powder. It is insoluble in water and dilute acids, but dissolves in ammonium tartrate to a violet solution and in oxalic acid to a blue solution. Even dilute alkalies decompose it, forming a gelatinous reddish mass of hydroxide, while when heated it leaves a brown residue soluble in acid to a yellow liquid.

The purest forms bear the commercial name of *Paris blue.* When precipitated in presence of gypsum, alum, barium sulphate, chalk, etc., it forms *mineral blue* of paler colour. When obtained by pouring a ferric salt into excess of potassium ferrocyanide it forms *Prussian blue soluble in water* (insoluble in salt solutions or in water at 80°), and this, mixed with indigo carmine, yields *night blue,* which does not change in colour even in artificial light. The name *soluble Prussian blue* is given also to a solution in oxalic acid.

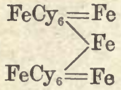
Prussian blue varies in price from £32 to £44 per ton and Paris blue from £120 to £220. *France* exported 117 tons in 1913 and 70 in 1915.

POTASSIUM FERRICYANIDE : K_3FeCy_6 (Red Prussiate of Potash). On passing chlorine into, or electrolysing, a solution of potassium ferrocyanide this is oxidised with formation of potassium ferricyanide, which separates in red rhombic crystals with a greenish reflection :

$$2K_4FeCy_6 + Cl_2 = 2KCl + 2K_3FeCy_6.$$

When heated in the air, the ferricyanide blackens and colours the flame purple owing to the formation of cyanogen. It dissolves easily in water, but is insoluble in alcohol. On adding a solution of potassium ferricyanide to a solution of a ferrous salt, a bright blue precipitate of ferrous ferricyanide is formed, which is called *Turnbull's blue.* This is a sensitive reaction for ferrous salts, whilst with ferric salts no precipitate (only browning) is formed :

$$2K_3FeCy_6 + 3FeSO_4 = 3K_2SO_4 + \overset{\cdot\cdot}{Fe}_3\overset{\prime\prime\prime}{Fe}_2Cy_{12}, \text{ that is,}$$



$$\begin{matrix} FeCy_6{=}Fe \\ \quad\quad >Fe \\ FeCy_6{=}Fe \end{matrix}$$

This precipitate does not dissolve in acids, but is decomposed by hot alkalis with formation of potassium ferricyanide and ferrous hydroxide, which immediately transforms the potassium ferricyanide into potassium ferrocyanide :-

$$(a) \qquad Fe_3Fe_2Cy_{12} + 6KOH = 3Fe(OH)_2 + 2K_3FeCy_6$$
$$(b) \quad 2K_3FeCy_6 + 2Fe(OH)_2 + 2KOH = 2K_4FeCy_6 + 2Fe(OH)_3$$

Commercial Prussian blue contains large amounts of Turnbull's blue.

Red potassium prussiate is poisonous. It is used for the production of pigments, and in dyeing and printing. It costs about £140 per ton.

POTASSIUM PERFERRICYANIDE, $K_2[Fe(CN)_5,H_2O]$ (Black Potassium Prussiate), was prepared pure by Skraup, and its constitution was elucidated by L. Cambi in 1910, by showing its analogies with **Sodium Ferriaquapentacyanide, $Na_2[Fe(CN)_5, H_2O]$,** which was produced by K. A. Hofmann from the nitroprusside. The formation of the perferricyanide by the action of chlorine takes place according to Cambi as follows :

$$[\overset{III}{Fe}\,(CN)_6]''' + Cl_2 + H_2O = [\overset{III}{Fe}(CN)_5,\, H_2O]'' + Cl' + CN{\cdot}Cl.$$

SODIUM NITROPRUSSIDE : $FeCy_5(NO)Na_2, 2H_2O$. This is a very sensitive reagent for alkali sulphides and various organic substances, with which it acquires an intense violet colour; it is obtained in red crystals from a solution of sodium ferrocyanide with nitric acid.

CALCIUM FERROCYANIDE : $FeCy_6Ca_2$. This compound is obtained in the course of gas manufacture (*see above*) when the preparation of potassium ferrocyanide is not desired. It crystallises with $12H_2O$ and loses $11\frac{1}{2}H_2O$ at 40°. It is used for the preparation of the corresponding potassium salt and of other cyanides (*see above*).

NICKEL: Ni, 58.68

Nickel is sometimes found native in meteorites, but abounds in *Nickeline*, $NiAs_2,NiS_2$, in *Nickel Arsenide*, NiAs, but most abundantly in the form of *Garnierite*, a mixed silicate, $2(Ni,Mg)Si_4O_{13},2H_2O$, which is found in large quantities in Nova Scotia (whence all the ore is exported to Germany, France and England) and in Norway (in the Sotersdalen valley, near Christiansand) and contains 10 to 20 per cent. of nickel. Nowadays 60 per cent. of the world's output is furnished by Canada (Sudbury, Ontario), which has rich deposits of mixed nickel and copper ore. The nickel is obtained from this silicate by heating it with coke and a basic flux and then puddling in an open-hearth furnace (p. 823) with hot air in order to separate the Fe, Mn, and Si in the form of a slag and obtain free nickel; magnesium is finally added in order to eliminate all the oxygen, the presence of which is very disadvantageous. In the extraction of nickel from metallic sulphides, the fact is made use of that nickel has more affinity for sulphur than has iron, but less affinity than copper, whilst the affinities of these metals for oxygen are in the reverse order. These ores, which often contain copper and iron, are first roasted and then smelted until a matte (p. 694) is formed containing much nickel (40 per cent. Ni, 40 per cent. Cu). On repeatedly roasting and smelting this then forms crude nickel, the treatment being similar to that of copper (p. 694). The nickel is finally refined in a Bessemer converter (p. 821). A new and important process is that of L. Mond, 1889, which has been used since 1902 in Canada and at Clydach (South Wales), and by which 400 or 500 tons of ore may be treated daily (in 1910 1800 tons of nickel were produced, and since then the output has increased). The regulus, containing 80 per cent. of nickel, as obtained in the Bessemer converters, is then treated in England by the Mond-Langer process, which consists in first reducing the regulus at 300° with water-gas in a tower, and then charging the product into a "volatiliser," into which a current of carbon monoxide at 100° is passed. Nickel tetracarbonyl, $Ni(CO)_4$, is thus formed, which is volatile and passes into the decomposition tower, where at 180° all the nickel is separated of 99·9 per cent. purity; formerly only 94 per cent. nickel was obtained. Nickel is also obtained from alloys and from the regulus by electrolytic means, using the alloy itself as an anode in a bath of copper and nickel chlorides and collecting the copper on a copper cathode. The nickel which remains in the concentrated solution is separated from copper, and also from iron, by H_2S. The solution is then electrolysed with an anode of carbon and a cathode of copper, on which the nickel collects.

Pure nickel has a silvery appearance, is as ductile as copper, but tougher, and is feebly magnetic. It has a specific gravity of 8·9 and melts at 1435°; at 2100° it dissolves as much as 6·4 per cent. of carbon. It is unalterable in the air and dissolves with difficulty in hydrochloric and sulphuric acids, but easily in nitric acid. It is a constituent of various alloys,[1] as in nickel coinage, which contains 75 per cent. of copper and 25 per cent. of nickel, in *German silver* or *pinchbeck*, which is used in the preparation of electrical resistances on account of its low conductivity, and contains 50 per cent. Cu, 25 per cent. Ni, and 25 per cent. Zn (p. 700), and in *invar*, which contains 63 per cent. Fe, 36 per cent. Ni, 0·5 per cent. C and 0·5 per cent. Mn, and is used for scientific instruments, owing to its low coefficient of thermal expansion. It is also much used for nickel-plating[2] (pp. 521 *et seq.*), in the manufacture of many

---

[1] A. Bianchi and E. Di Nola (1910) give the following test for traces of nickel. The object to be tested is moistened with a drop of concentrated hydrochloric or nitric acid, the drop being afterwards absorbed by a strip of filter-paper, which is then exposed to the action of ammonia vapour and moistened with a drop of acetic acid and one of dimethylglyoxime (saturated solution): in presence of nickel a red solution is formed (the presence of copper or iron does not affect the test).

[2] **Galvanoplastics and Electro-plating.** In 1805 Brugnatelli succeeded in gilding silver coinage electrolytically, and in 1836 Elkington in Birmingham attempted to replace the usual method of gilding silver articles in a furnace by the use of baths of gold chloride and potassium bicarbonate, but the gilding obtained in this way was very thin. In 1873 Jakobi at St. Petersburg invented an ingenious process of reproducing medals and artistic objects by producing an exact mould of these by means of wax or plaster and then coating every detail of the surface of these moulds with very fine graphite and thus rendering it electrically conductive. He then suspended the mould from the negative pole (cathode) of an electrolytic bath containing a suitable metallic

laboratory utensils, and for other purposes, but about two-thirds of the world's production is used in the manufacture of nickel-steel armour-plates. In a finely divided state it is used as a catalyst, especially in presence of sodium hydroxide. Autogenous welding is difficult, as in the hot nickel absorbs large amounts of gas, which are liberated when it solidifies, leaving a spongy mass; welding is therefore effected with the hammer at not too high a temperature, as is done with iron.

STATISTICS. The world's production of nickel in 1892 was 2968 tons; it was 9850 tons in 1903 and 14,100 tons in 1906, of which 6500 tons were produced in the United States and Canada and 2600 tons in Germany; in 1912 the world's production was 26,500 tons.

The *United States* imported 14,000 tons of nickel in 1911, 20,000 in 1912, and 23,000 in 1913, 13,500 tons (£1,960,000) being exported in 1913. The nickel ore imported amounted to 18,600 tons in 1909, 28,600 in 1910, 24,000 in 1911, 34,000 in 1912, and 38,500 (£1,320,000) in 1913. The United States produces scarcely any nickel, this being supplied almost exclusively by Canada. *Norway* in 1908 produced 81 tons of nickel and somewhat larger quantities since then.

In 1912 *Germany* imported about 15,000 tons of nickel ore and 2142 tons of the metal (in 1909 3745 and in 1913 3416 tons), the exports being 2555 tons of nickel in 1912 and 2409 in 1913 (1635 in 1909).

France imported 10,293 tons of nickel ore in 1913, 28,580 in 1914, and 19,000 in 1915.

The production of nickel in *Europe* is largely from imported ore, this coming especially from Nova Scotia.

The output of nickel in different countries is as follows (tons):

	1900	1905	1908	1909	1912
Germany	1,400	2,700	2,600	4,500	—
France	1,700	2,200	1,400	1,500	—
England	1,500	3,100	2,800	3,500	—
United States and Canada .	3,000	4,500	6,000	10,000	—
Whole world . . .	7,600	12,500	12,800	20,000	26,500

---

salt and formed the positive pole of the same metal; on passing an electric current through this bath the mould became coated with very fine particles of the metal, forming a continuous and compact surface; the metal forming the anode was gradually dissolved in the bath as fast as it was deposited on the cathode. This method was improved by Spencer of Liverpool and then by Delarive of Paris. In 1840 the latter succeeded in gilding copper and brass articles. Thus galvanoplastic methods were no longer limited to the reproduction of objects, but the art of *electro-plating* was evolved by means of the generalisations introduced, and applied industrially by Ruolz in 1842, so that the most varied metals could be covered with layers of any desired thickness of another metal. It was at this period and by utilising this process that the celebrated firm of Christofle was started in Paris and the firm of Elkington Bros. in Birmingham in 1844. These enterprises were quickly followed by numerous others of a similar character in various countries.

In 1843 Böttger had already perfected the process of platinising by employing a bath of ammonium platinichloride and ammonia. In 1878 he proposed the use of a bath of ammonium platinichloride and sodium citrate, which is still used to-day. The first industrial form of nickel-plating is also due to Böttger, who succeeded in 1843 in devising a process by the use of a bath of the double sulphate of ammonium and nickel. This bath was improved by Planzan in 1875 by the addition of citric acid, and still further by Weston in 1879, who obtained perfectly white, homogeneous nickel deposits by replacing the citric acid by boric acid. In 1897 Förster succeeded in preparing thick nickel deposits from hot baths of nickel sulphate. Black nickel-plating is obtained if, after the object has been immersed for an hour in the bath at 3·5 volts, the voltage is suddenly lowered to 0·25.

The electrolytic deposition of iron presented greater difficulties, and the attempts of Böttger and of Ryhiner in 1848 did not lead to practical results, whilst, on the other hand, great hopes were awakened by the work of Feuquières in 1867, and still more by that of Lenk in 1869, who used a bath of magnesium sulphate and iron sulphate in presence of basic magnesium carbonate.

Attempts were also made by Ruolz and by Jakobi to obtain metallic alloys electrolytically by the use of baths containing mixtures of various metallic cyanides, but they were without industrial results. The process has only become important and practical since 1895, when Jordis replaced the cyanides by lactates, that is by solutions of the metals in lactic acid; these gave good, adherent deposits free from scales in the case of thin coatings, but for thicker deposits better results are obtained with metallic salts of ethylsulphuric acid, as proposed by Langbein.

Italy imported 525 tons (£72,000) of nickel and its alloys in 1909, 1585 in 1911, 1725 in 1912, 1200 in 1913, 1112 in 1914, 1813 in 1915, 2091 in 1916, and 3294 in 1917.

The *price* of nickel was about 12*s.* per kilo in 1870 and rose to £1 9*s* in 1875, owing to the use of nickel coinage in Germany. After the discovery of the metal in Nova Scotia it fell to 16*s.*, subsequently to 4*s.*, and then, in about 1910, to 2*s.* 4*d.* During the European War the price rose to 6*s.* and on occasions to 16*s.* per kilo.

NICKEL OXIDES : NiO and Ni_2O_3. These are similar to the oxides of cobalt, although nickel compounds all correspond with **Nickelous Oxide,** in which the nickel is divalent. This oxide is formed on heating the hydroxide or the nitrate and is found in nature in green crystals as *bunsenite.* **Nickelic Oxide, Ni_2O_3,** is formed by the action of a hypochlorite on a nickel salt, or on gently heating the nitrate or chlorate. It is a black powder which is transformed into NiO on heating.

NICKEL HYDROXIDE, $Ni(OH)_2$, is formed as a green precipitate by the action of KOH on a nickel salt. It dissolves in NH_3 to form a blue solution.

NICKEL CHLORIDE : $NiCl_2$. This is obtained on dissolving nickel in aqua regia. It crystallises from water in green crystals containing $6H_2O$. On heating, these lose water and become yellow. It costs 3*s.* 4*d.* per kilo.

NICKEL SULPHATE : $NiSO_4$. This compound is formed on dissolving nickel or its hydroxide in H_2SO_4. It crystallises at 15° to 20° with $7H_2O$ in bright emerald-green crystals, isomorphous with crystals of $MgSO_4$, whilst at higher temperatures it crystallises with $6H_2O$ in bluish-green crystals. At 280° it loses all its water and becomes yellow. It dissolves in 3 parts of water and is often used in nickel-plating. It costs about £48 per ton. Germany produced 220 tons in 1905.

NICKEL AMMONIUM SULPHATE : $NiSO_4,(NH_4)_2SO_4,6H_2O$. If a solution of ammonium sulphate is added to a solution of $NiSO_4$ in water acidified with H_2SO_4, green crystals of this double salt separate on concentration. It is only slightly soluble in water (2 : 17). This salt is also used for nickel-plating, and costs £40 per ton.

NICKEL SULPHIDE : NiS. This is obtained from soluble salts with alkali sulphides, though not by passing H_2S into acid solutions, as it is soluble in acids; as obtained from alkali sulphides it does not, however, dissolve in acids, perhaps because it is polymerised. When freshly precipitated it is soluble in alkali sulphides, but becomes insoluble after a short time.

NICKEL TETRACARBONYL : $Ni(CO)_4$. This compound is now of industrial importance as it is used in the preparation of nickel by the Mond process (*see above*), and is formed on passing CO over powdered nickel. It is a colourless liquid which boils unaltered at 43° and burns with a smoky flame. It is solid at — 25°. Its vapours explode at 160° with separation of Ni and CO.

NICKEL CYANIDE, $Ni(CN)_2$, is formed as a green precipitate when KCN is added to a solution of a nickel salt, but it is easily soluble in an excess of KCN, forming **Potassium Nickelocyanide, K_2NiCy_4,** which is unstable and is decomposed by HCl.

COBALT: Co, 58.97

This metal is less abundant and less used than nickel. It is found in nature, especially in *Cobaltine,* $CoAs_2,CoS_2$ (which contains up to 34 per cent. Co), and in *Smaltine,* $CoAs_2$ (3 to 28 per cent. Co). Other less abundant ores are: *asbolite* (oxide of cobalt and manganese, containing 2 to 20 per cent. Co and abounding in Nova Scotia and New South Wales), *linneite* (cobalt sulphide with nickel and iron sulphides; it sometimes contains 40 per cent. Co and much nickel), *red cobalt* (hydrated cobalt arsenate, containing up to 39 per cent. of cobalt oxide). When treated with strong acid or with aqua regia, cobalt ores usually give red colorations. The ores are usually first roasted in a current of air to obtain the oxide. The most important deposits of cobalt were in Nova Scotia, but since 1904 the abandoned deposits of Canada (Ontario), containing also silver, have been largely worked. Smaller amounts are found in Scandinavia, Saxony, Bohemia, Thuringia, and the Harz.

The metal is extracted in the same way as nickel, and is often found in company with it. In order to separate cobalt from solutions of nickel they are treated with potassium nitrite, by which means the cobalt only is precipitated. The metal is also obtained by reducing the oxide, Co_3O_4, with charcoal or hydrogen or CO, and in a less pure condition by the alumino-thermic process (p. 727).

The pure metal is lustrous, with a reddish reflex. It has a specific gravity of 8·5, does not alter in the air and is less magnetic than iron, but remains magnetic at 1100°. It melts at about 1467°, and by the addition of very small amounts of Mg it may be obtained in compact and very hard masses. It dissolves slowly in HCl or H_2SO_4, whilst it dissolves immediately in HNO_3, forming cobalt nitrate.

P. Weiss and Herber-Kalmus (1913) have prepared a cobalt-iron alloy, Fe_2Co, which in powerful magnetic fields has a magnetic permeability ten times that of the best soft Swedish iron.

With chromium cobalt gives an alloy which can be drawn out into good wires for thermo-cells, oxidises more difficultly than nickel-chromium wire in the hot, and has a higher melting-point. Small proportions of cobalt added to pure iron produce an extraordinary resistance to corrosion in general and the use of sheet iron for roofing is prophesied. Cobalt deposited electrolytically on steel and brass is more adherent than nickel and also has a more silvery appearance; it also allows of the use of greater current density with more concentrated solutions and more rapid deposition. Cobalt is harder than nickel (165 instead of 65 on Brinell's scale), and when introduced in the proportion of 15 per cent. into steel containing small percentages of chromium and tungsten or molybdenum, it forms very hard alloys which serve excellently for rapid cutting tools. Pure cobalt has compressive and tensile strengths greater than other pure metals. Nova Scotia in 1907 exported 3943 tons of cobalt ore. The *price* of cobalt is £1 8*s.* to £1 12*s.* per kilo, with a tendency to fall.

The more ordinary cobalt compounds contain a divalent cation $Co^{\cdot\cdot}$ and correspond with cobaltous oxide, CoO; the other derivatives correspond with cobaltic oxide, Co_2O_3. Ionised cobaltous salts are red, whilst when not ionised they are blue. A solution of $CoCl_2$ is red because it is highly ionised, whilst if HCl is added the ionisation is diminished and it becomes blue. Sympathetic inks may thus be prepared, as when used for writing on red paper the characters cannot be seen, whilst they become blue on warming the paper.

The value of the cobalt ores mined in Canada, which have been the subject of much financial speculation, amounted to about £1,520,000 in 1906.

COBALTOUS OXIDE : CoO. This is a brown powder which is formed on heating the hydroxide or carbonate out of contact with the air.

Cobalt Enamels are alkali silicates coloured blue by CoO or other colours by mixtures of cobalt oxide with other oxides, such as ZnO, etc.

COBALTOUS HYDROXIDE : $Co(OH)_2$. This is obtained as a red precipitate by the action of KOH on cobaltous salts in the absence of air, as in presence of air it is easily oxidised.

COBALTOUS CHLORIDE : $CoCl_2$. When cobalt is dissolved in hydrochloric acid, crystals of $CoCl_2 + 6H_2O$ of a deep red colour separate from the solution. On heating, these lose water and become blue.

COBALT SULPHATE, $CoSO_4$, is analogous to nickel sulphate. It forms dark red monoclinic crystals containing $7H_2O$, isomorphous with $FeSO_4$, and also forms double salts with alkali sulphates, such as $K_2SO_4,CoSO_4,6H_2O$.

COBALT NITRATE, $Co(NO_3)_2$, crystallises with $6H_2O$ in bright red prisms very soluble in water, which are hygroscopic. It is obtained by dissolving the oxide or carbonate in nitric acid. It melts below 100°, forming a violet and then a green mass, and at a high temperature is converted into black oxide.

COBALT SILICATE has an intense blue colour and is used in the preparation of coloured glass and enamels, whilst when powdered it is used in painting. By heating alumina to a white heat for some time with a cobalt salt (especially the phosphate), *Thenard's blue* is obtained, which is of various shades of blue according to the proportions of Co and Al present, and in artificial light appears violet; it is insoluble in acids or alkalies and is not changed by calcination; it is consequently used for colouring porcelain, glass, etc., and for painting frescoes in oils. It costs 4*s.* 8*d.* to 5*s.* 6*d.* per kilo.

COBALTIC OXIDE : Co_2O_3. This is a black powder which is formed on calcining cobalt nitrate at a moderate temperature. At higher temperatures it is transformed into **Cobaltous-cobaltic Oxide, Co_3O_4,** and if the temperature is raised still further CoO remains.

On treating Co_2O_3 with hydrochloric or sulphuric acid the corresponding cobaltic salts are not formed, but cobaltous compounds are produced with evolution of oxygen, chlorine, etc. **Cobalt Alums** may, however, be obtained by dissolving this oxide in cold dilute sulphuric acid and then adding alkali sulphates.

POTASSIUM COBALTICYANIDE : $CoCy_6K_3$. This compound crystallises in colourless rhombic prisms which have a constitution corresponding with that of red potassium prussiate.

COBALTIPOTASSIUM NITRITE : $Co(NO_2)_3,3KNO_2,1\frac{1}{2}H_2O$. This is obtained in the form of somewhat insoluble yellow crystals by adding potassium nitrite and acetic acid to a cobaltous salt. It is used for separating nickel from cobalt, as on increasing the number of potassium ions it becomes almost insoluble.

COMPLEX AMMONIUM SALTS. On adding ammonia to cobaltous salts until the precipitate first formed is redissolved a solution is obtained which absorbs oxygen from the air, and if to this an acid corresponding with the cobaltous salt employed is added, a brick-red crystalline powder separates which is known as a *roseocobalt* salt. Thus, according to the salt employed, roseocobaltic chloride, $CoCl_3(NH_3)_5 . H_2O$, or roseocobaltic nitrate, $CO(NO_3)_3(NH_3)_5 . H_2O$, is obtained. If these roseocobalt salts are heated with a little acid they acquire a purple-violet colour, forming salts of *Purpureocobalt*, such as $CoCl_3(NH_3)_5$ or $Co(NO_3)_3(NH_3)_5$.

If ammonium chloride and an oxidising agent are added to an ammoniacal solution of cobalt chloride, reddish-yellow crystals of $CoCl_3(NH_3)_6$ separate, which are soluble in cold water; compounds of this type are called *luteocobalt* salts. By suitably varying the groups with other acid radicals, such as NO_2, etc., *Croceocobalt, Flavocobalt,* and *Xanthocobalt* salts are formed.

Platinum, chromium, and copper also form compounds similar to those just described, but differing according to the valencies of these metals. In compounds containing the *Hexammino* group, $(NH_3)_6$, some of the molecules of NH_3 may be either replaced by water molecules or simply eliminated; there are thus five series of salts (X indicates the acid radical): *Hexamminocabalt* salts or *Luteocobalt* salts, $CoX_3(NH_3)_6$, *Pentamminocobalt* salts or *Purpureocabalt* salts, $CoX_3(NH_3)_5$, *Tetramminocobalt* or *Praseocabalt* salts, $CoX_3(NH_3)_4$, and *Triamminocabalt* salts, $CoX_3(NH_3)_3$.

These salts do not show the ordinary reactions for cobalt and ammonia, and we must, therefore, suppose them to contain complex ions. They are more or less ionised by water; thus, for example, all the chlorine may be removed from luteocobalt chloride, $CoCl_3(NH_3)_3$, by means of silver nitrate, from which we may infer that the three atoms of chlorine form the anion and that the trivalent cation will be formed by the group $Co(NH_3)_6^{\cdots}$, so that we have a quaternary electrolyte with three anions and one associated cation. When 1 mol. of ammonia is eliminated, 1 atom of chlorine loses its property of being ionised; therefore the solution conducts the current less well and only 2 atoms of chlorine are separated by silver nitrate, that is, a ternary electrolyte is formed. On eliminating a further molecule of NH_3 the conductivity is still further diminished and only a single atom of chlorine remains ionised, so that we now have a binary electrolyte. If, finally, a third molecule of ammonia is removed we obtain triamminocobalt chloride, $Co(NH_3)_3Cl_3$, which is no longer ionised and therefore no longer conducts the electric current.

By placing the dissociated anion, X, within square brackets, we obtain the four following general formulæ, in which M represents the fundamental metal, Co, Pt, Fe, etc., round which the other groups are attached, the number of which (*co-ordination number* of Werner) attains a maximum of 6 (Co = 6; C = 4; N = 4; B = 4, etc.), whilst the other groups or ionised atoms are indirectly united to the fundamental metal:

$$[M(NH_3)_6]X_3; \quad [M(NH_3)_5X]X_2; \quad [M(NH_3)_4X_2]X; \quad [M(NH_3)_3X_3].$$

If now we commence to increase the number of negative groups or atoms (Cl, NO_3, Cy, OH, etc.) at the expense of the NH_3 groups, we obtain new negative complexes the valency of which is given by the number of new groups introduced; thus we have, for example, tetramminocobaltipotassium nitrite, $[Co(NH_3)_2(NO_2)_4]'K^{\cdot}$, and we might also obtain the compound, $[Co(NH_3)(NO_2)_5]''K_2^{\cdot\cdot}$, which has not yet been prepared, and finally we might obtain the compound $[Co(NO_2)]_6'''K_3^{\cdots}$, *i. e.*, **Cobaltipotassium Nitrite**, which is well known and which may be compared with potassium ferricyanide, $Fe^{\cdots}Cy_6K_3$. None of these compounds show the reactions of the NO_2 residue, because this is not ionised and is united directly to the fundamental metal Co. When the metal is divalent we obtain compounds of the type $M^{\cdot\cdot}(NH_3)_6X_2$ (where M indicates the divalent metal) which correspond with the compound $[M^{\cdot\cdot}Cy_6]^{''''}X_4^{\cdot\cdot\cdot\cdot}$, if NH_3 is replaced by various other groups such as cyanogen. A well-defined salt corresponding with this group of compounds is potassium ferrocyanide, $Fe^{\cdot\cdot}Cy_6K_4$.

Light was thrown on the constitution of these very numerous complex compounds of cobalt, platinum, etc., by the work of Werner and of his pupils, especially Miolati. The number of these compounds which are now known is about 2000, and until lately it had not been possible to interpret their constitution in any rational manner.

For example, two isomeric compounds, $Pt(NH_3)_4SO_4(OH)_2$, are known, of which, although they have the same atomic composition and the same molecular weight, the one behaves as a strong base and gives no reaction for the SO_4'' ion in aqueous solution (no precipitate with $BaCl_2$), whilst the other behaves as a neutral salt and precipitates $BaSO_4$ with $BaCl_2$. The former is thus a hydroxide of *Sulphatotetramminoplatinum* of the following constitution $[SO_4Pt(NH_3)_4](OH)_2$, whilst the latter is a sulphate of dihydroxyltetramminoplatinum, $[(OH)_2Pt(NH_3)_4]SO_4$.

The crystallised hexamminic salts in which several molecules of ammonia are replaced by 1 to 6 molecules of water are also interesting. In some of these the molecular conductivity is only slightly influenced (Jörgensen), for instance, $[Co(NH_3)_4(H_2O)_2]Br_3$, $[Co(NH_3)_5H_2O]Br_3$, and $[Co(NH_3)_6]Br_3$, whilst in others one acid residue ceases to be ionised for each molecule of water introduced, and in others again for each molecule of water introduced one acid residue is ionised, and is placed outside the square brackets in the following formulæ, which show the 3 hydrates of trichlorotriamminocobalt $[Co(NH_3)_3Cl_3]$:

$[Co(NH_3)_3(H_2O)Cl_2]Cl$;	$[Co(NH_3)_3(H_2O)_2Cl]Cl_2$;	$[Co(NH_3)_3(H_2O)_3]Cl_3$
Dichloroaquotriammino-cobalt chloride	Chlorodiaquotetrammino-cobalt dichloride	Triaquotriammino-cobalt trichloride

In these *aquo salts* we also find cases of *isomerism of hydration* with which various colorations correspond, and their constitution is explained by stereochemical considerations which are developed in the second volume of this work (" Organic Chemistry "). Complex salts of this character are also known containing several fundamental and stable condensed nuclei which are not broken up either by ionisation or by spontaneous hydrolysis.

(*b* and *c*) PLATINUM GROUP

This is divided into two sub-groups :

	LIGHT METALS		
	Ruthenium, Ru	Rhodium, Rh	Palladium, Pd
Atomic weight . .	101·7	102·9	106·7
Specific gravity . .	12·26	12·1	11·9

	HEAVY METALS		
	Osmium, Os	Iridium, Ir	Platinum, Pt
Atomic weight . .	190·9	193·1	195
Specific gravity . .	22·4	22·38	21·45

The valency of these elements varies considerably; thus in osmium it varies from 2 to 8 and in palladium from 1 to 4.

These metals are found naturally in the native state only, generally as mixtures in the island of Sumatra, California, Australia, the Ural Mountains, etc., and frequently together with iron and gold. The complete separation of these metals from one another is difficult because their salts have many properties in common and the impurities further complicate the processes of extraction and separation.

Generally speaking, by the action of aqua regia on a mixture of these minerals, a mixture of the chlorides, $PtCl_4$, $IrCl_4$, $RhCl_2$, and $PdCl_3$, is obtained, which on heating with NaOH forms $IrCl_3$ (from the $IrCl_4$) and sodium hypochlorite (which forms the chloride with alcohol). On then adding ammonium chloride ammonium platinichloride, $(NH_4)_2PtCl_6$, separates and yields spongy platinum on heating, whilst the chlorides of palladium and rhodium do not form insoluble double salts like platinum and are separated on further concentration. From the final mother-liquors the other metals are precipitated by iron turnings.

RUTHENIUM: Ru, 101.7

This is a brittle metal, very infusible (melting at about 2000°), and only dissolves slowly in aqua regia, being transformed into the chloride, $RuCl_3$, although if the ruthenium is alloyed with a little platinum it is much more easily dissolved. It forms several oxides, RuO, Ru_2O_3, RuO_2, and RuO_4 (peroxide) and several chlorides, $RuCl_2$, $RuCl_3$, and $RuCl_4$.

A compound is also known which has a certain similarity with potassium manganate, namely **Potassium Rutheniate, K_2RuO_4,H_2O**, which is formed on melting ruthenium with potassium nitrate and potassium carbonate. From the bright orange-coloured aqueous solution obtained from this melt black crystals separate. When a current of chlorine is passed through this solution it carries with it the volatile **Tetroxide, RuO_4**, which condenses on cooling in golden-yellow crystals. With dilute acids it forms **Potassium Per-rutheniate, $KRuO_4$**, which is analogous to $KMnO_4$, and forms intensely green solutions.

RHODIUM: Rh, 102.9

This element was discovered in 1803 by Wollaston, who prepared it from the **Chloropurpureorhodium Chloride, $Rh(NH_3)_5Cl_3$** (*see* p. 848). It has the appearance and ductility of silver and a specific gravity of 12·1. When pure it is not even attacked by aqua regia, but becomes soluble in that mixture when alloyed with platinum. When heated in the air it forms the oxide, RhO, and another oxide, Rh_2O_3, is also known, which forms salts with acids. It has the property of absorbing considerable quantities of hydrogen. On heating in a current of chlorine it forms the dark red **Trichloride, $RhCl_3$**, which forms double salts, and its sulphate also forms **Alums** with alkali sulphates. Rhodium is rare and very dear, costing 14*s.* per gram in 1905, 3*s.* in 1909, and 12*s.* in 1910.. It is now used in the construction of extremely sensitive *electrical pyrometers*, which may be used up to a temperature of 1600°. These pyrometers are constructed of two wires, one of platinum about 0·6 mm. thick and 150 cms. long, and the other of platinum alloyed with 10 per cent. of rhodium. The two wires are melted together at one extremity and thus form an element which, when connected at the two other extremities with a galvanometer, gives rise to a feeble current as the temperature of the junction is raised (an E.M.F. of 0·001 volt for each 100°). The E.M.F. produced is exactly proportional to the temperature and is indicated by the galvanometer with an error not exceeding 5° at 1000°. The galvanometer may be placed at a long distance from the source of heat by connecting it to the pyrometer by ordinary electric leads, and it is thus possible to observe the course of temperature changes in a furnace at any moment even from a distance.

PALLADIUM: Pd, 106.7

This element is found in nature alloyed with gold or in certain ores with selenium. It has a silvery appearance, a specific gravity of 11·8, and a melting-point of 1700°.

It is dissolved by concentrated boiling strong acids. On heating it first forms an oxide which decomposes at still higher temperatures. The most significant and characteristic property of palladium is that of absorbing in the cold (but after previous heating to redness) 661 times its own volume of hydrogen gas at 20°, 117 at − 50°, 880 at 0°, 735 at 40°, 750 at 80°, and 800 volumes at 100°, when it is finely divided (palladium sponge). If palladium foil is used as a cathode in the electrolytic decomposition of water it is capable of absorbing 960 volumes of H, which it evolves completely on heating *in vacuo.* Hydrogen so absorbed by palladium has very energetic reducing properties; it reduces ferric to ferrous salts, and transforms Cl into HCl; its action appears to be based on a catalytic phenomenon. Palladium forms a chemical compound, Pd_2H, with hydrogen, which has a constant dissociation pressure and is capable of dissolving a further amount of hydrogen until an alloy, Pd_3H_2, is formed (*see* "Hydrogen," p. 136).

Owing to the great increase in the price of platinum during the European War (*see above*), alloys of 80 per cent. Au and 20 per cent. Pd were used to replace platinum for many purposes.

The *price* of palladium was formerly 4*s*. per gram, but during the war it rose to 14*s*. in 1916 and to 17*s*. in 1917.

In its compounds palladium is sometimes divalent and sometimes tetravalent; it is divalent in its more stable compounds.

It forms **PALLADIOUS IODIDE,** PdI_2, as insoluble black crystals by the action of palladious chloride on KI. This reaction is used for the separation of iodine from Cl and Br, the latter forming soluble palladium compounds.

PALLADIOUS CHLORIDE, $PdCl_2$, is obtained by evaporating a solution of palladium in aqua regia and forms brownish-red crystals containing $2H_2O$. Its solution is used for the qualitative and quantitative determination of CO.

PALLADIC CHLORIDE, $PdCl_4$, is not known in the free state because it immediately decomposes into $PdCl_2 + Cl_2$. It is, however, known in the form of slightly soluble double salts, such as K_2PdCl_6 and $(NH_4)_2PdCl_6$.

OSMIUM: Os, 190.9

This element has the highest specific gravity of all the metals, namely 22·48, and excepting chromium it has the highest melting-point, about 2500°. When massive it is not dissolved even by aqua regia, whilst when finely divided it dissolves in various mineral acids.

Before 1900 osmium cost 4*s*. per gram, but it is now used in electric lamps, and the price has risen to 8*s*. per gram, as it is only found in very small quantities in nature. (*Translator's note.*—Various metals are now known to have a still higher melting-point than osmium.)

OSMIUM OXIDES. Various oxides are known, namely OsO, Os_2O_3, and OsO_2, but the most important is OsO_4, which is formed on heating powdered osmium in the air or in steam, or on treating osmium with HNO_3, aqua regia, or moist chlorine. It forms a colourless, crystalline mass which sublimes in needles, melts easily and boils at about 100°. The vapours have an irritating smell and are highly poisonous. This oxide is commercially known as *osmic acid*, but its aqueous solution shows neutral reaction and it does not form salts. It is used in microscopy, as it easily separates osmium as a black powder when reduced by organic matter. It was employed by Auer for the new incandescent *osmium lamp*. This electric lamp was prepared with filaments obtained by squirting a paste formed of an adhesive substance mixed with osmium oxide through a very fine hole. These filaments were used instead of carbon filaments in an ordinary evacuated electric lamp, and on passing the current the oxide was reduced to metallic osmium, which resists the highest temperatures *in vacuo*. Such lamps show the advantage that for an equal time (1000 hours) and equal consumption of electrical energy, they produce a quantity of light almost double that of the ordinary incandescent lamp, but they can only be used on low-voltage circuits (50 volts or preferably 25 volts), although they are now also adapted to ordinary circuits at 120 volts by means of a distributor which divides the current into three portions at 40 volts each.

The glass bulb of this lamp does not blacken even after prolonged use, and it can therefore be used at maximum efficiency to the end. The temperature of the filament does not exceed 1450°, whilst that of the carbon filament is as high as 1600°. The advantage obtained is therefore due to the more intense light emitted by the osmium filament.

In 1893 the first important experiments on this lamp were conducted, and a great future was prophesied for it. It is, however, possible that an insufficient amount of osmium will be found on the earth's surface to satisfy the demand.

Before the war the oxide cost 5*s*. 7*d*. per gram.

(*Translator's note.*—The osmium lamp is now obsolete, having been replaced by other metallic-filament lamps.)

POTASSIUM OSMIATE, K_2OsO_4. On melting osmium with potassium carbonate and potassium nitrate, this compound is obtained in a similar manner to the corresponding ruthenium compound. It crystallises in violet octahedra, containing $2H_2O$.

Several chlorides are known, such as $OsCl_3$ and $OsCl_4$, which are similar to the corresponding ruthenium chlorides.

IRIDIUM: Ir, 193.1

Iridium and osmium are extracted in Russia from the residues left after working up platinum, but the amounts prepared are diminishing: 4495 kilos in 1902, 1730 in 1909, and 1620 in 1910.

This element melts at a slightly lower temperature than ruthenium. It is separated from admixture with osmium by heating it in the air so that the osmium is volatilised as oxide. In the compact state it is not dissolved even by aqua regia, and its resistance to chemical reagents is also communicated to other metals with which it is alloyed, such as osmium and platinum. It is, therefore, used in the manufacture of crucibles, capsules, and other chemical apparatus, alloyed with 90 per cent. of platinum. In the massive state it is brittle in the cold and has a specific gravity of 22·42. In the spongy state its specific gravity is 15·8. The price of iridium was £160 per kilo in 1908 and £320 in 1910.

Two chlorides, $IrCl_3$ and $IrCl_4$, and their double salts, $IrCl_3,3KCl,3H_2O$—which is soluble in water—and $IrCl_4,2KCl$—which is insoluble—are known.

$IrCl_4$ is black and dissolves in water with a bright red colour.

The oxide, Ir_2O_3, forms salts and also an alum.

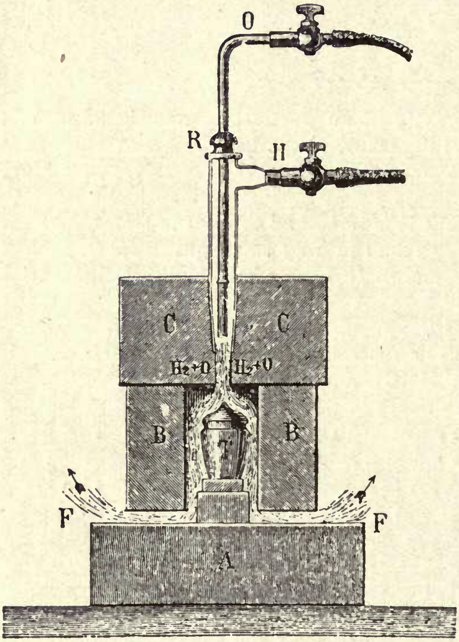


Fig. 328.

PLATINUM: Pt, 195

This metal is obtained almost entirely as small granules in sandy deposits in the Ural Mountains. On levigation this sand leaves a crude residue containing 75 to 85 per cent. of platinum and small quantities of 5 to 6 other metals of the platinum group, and sometimes gold, which is separated by amalgamation. The extraction and separation of the platinum are carried out by the methods already described above (p. 849), but whilst the sands from the Ural Mountains once contained up to 12 grams and more of platinum per ton, platinum-bearing sands are now treated which contain only 3 grams.

The *platinum sponge* which is obtained is converted into massive platinum by melting it in a refractory crucible arranged in a simple furnace heated by the oxy-hydrogen flame, as is seen in Fig. 328 (*see also* p. 191). The platinum thus melted at a high temperature is cast into bars of 3 to 5 kilos each, which are then hammered or drawn into sheets and thin wires for various commercial purposes; the wires may be as thin as 0·0001 mm. diameter.

The platinum thus prepared almost always contains iridium, which does not, however, depreciate its value. Its separation is not an easy matter, but after melting and slowly cooling, the platinum may be dissolved in aqua regia, leaving part of the unaltered iridium behind in a crystalline form. **Ammonium Platinichloride,** $(NH_4)_2PtCl_6$, may be precipitated from the solution with NH_4Cl, and on heating to redness leaves soft grey *spongy platinum* (capable of condensing much oxygen in its pores and then of igniting hydrogen, as in the Döbereiner lamp, p. 137). When treated with an alkali and a reducing agent (glucose, formaldehyde, alcohol, etc.), boiling solutions of platinum salts deposit a fine black powder, termed *platinum black. Platinised asbestos* is prepared similarly by steeping soft, long-fibred asbestos in a solution of a platinum salt and then reducing or calcining. Large quantities of these extremely finely divided forms of platinum are used in catalytic processes, *e. g.*, in making sulphur trioxide (*see* p. 332).

Pure platinum has a silvery appearance and is less hard and a poorer conductor of electricity and heat than copper.

It is one of the *noble metals* which are not altered by the air even on heating. In the cold it is very resistant to all chemical reagents, except aqua regia. On heating it is, however, attacked by the alkali hydroxides, by phosphorus, cyanides, sulphides, and the halogens; with Ag, Au, Sn, Sb, As, Cu, Pb, and Bi it forms easily fusible alloys. In order to avoid accidents in the laboratory, these substances should not, therefore, be heated in platinum apparatus. When pure it is attacked to some extent by boiling sulphuric acid, oxygen being liberated, but the presence of SO_2 or As_2O_3 or Sb_2O_3 prevents this action.

At a white heat it softens and may then be welded on to itself by prolonged hammering. It is very ductile and malleable, and may be drawn into very thin wires and foil. It has a specific gravity of 21·48. At about 1755° it commences to melt and at that temperature absorbs much oxygen, which is again liberated in the cold (spitting), as in the case of silver (pp. 512 and 710).

Platinum has been very largely used for the preparation of scientific and industrial apparatus since 1852, as after the studies of Deville in 1852 and Debray in 1857 this metal could be more easily purified, and worked and welded into any desired shape by the aid of the oxy-hydrogen flame.

Finely divided platinum (*platinum black*) absorbs considerable quantities of gases, such as H, O, CO, which are again liberated at a red heat. Sheets of red-hot platinum allow hydrogen but not other gases to diffuse through them.

Colloidal Solutions of Platinum (*see* p. 109) are obtained by passing an electric arc between two platinum electrodes under water. The particles of platinum are so fine that they pass through a filter.

The colloidal solution is black and is an active catalytic agent, even in very minute traces. It loses its catalytic properties, however, through the action of time and of heating and also through that of poisons, such as hydrocyanic acid or corrosive sublimate.

STATISTICS AND PRICES. Platinum is produced almost exclusively in Russia, in the Ural Mountains, where the output is about 6 tons per annum, which is 95 per cent. of the total world's production. This industry employs 15,000 to 20,000 workmen, and up to 1890 all the crude platinum obtained in Russia or elsewhere was acquired by the firm of Johnson, Matthey & Co. of London. This firm monopolised the refining of the product, containing 75 to 85 per cent. of Pt, and fixed the price. A considerable quantity of platinum is now refined in Germany. In 1899 a syndicate was formed, with head-quarters at Paris, which monopolised the world's production. In 1905 this amounted to 7 tons.

The production of platinum in Russia in 1840 was 1·5 ton and in 1860 0·99 ton. It was 2·9 tons in 1880, 7·306 tons in 1902, 5·506 in 1912, 7·775 (crude) in 1913, 4·875 in 1914, 3·354 in 1915, and 1·832 in 1916. *France* imported 5·05 tons of platinum in 1913, 2·9 tons in 1914, and 0·36 ton in 1915, the exports being 1·294 ton in 1913, 1·247 ton in 1914, and 0·64 ton in 1915.

Columbia produced 34 kilos in 1908, 50 in 1910, 205 in 1912, 466 (crude) in 1913, and 543 in 1914. *New South Wales* in 1913 produced 39·6 kilos and in 1914 38·8, and the *United States* 15 kilos in 1913 and 17·7 in 1914 (besides 90 kilos of refined metal obtained from native and foreign ores). One-third of the platinum produced is used for chemical industries and one-third each for jewellery and dental purposes. In 1910 *England* imported platinum to the value of nearly £280,000, but these official statistics are lower than the actual production, because it has been calculated that about 25 per cent. of the metal is stolen during treatment. The *price* was £35 per kilo in 1860, £20 in 1880, £40 in 1890, £100 in 1900, £136 in 1904, £256 in 1906, £200 in 1907, £160 in 1908, about £140 in 1909, and £224 in 1910. During the European War the price of platinum rose enormously owing to diminished production in Russia and to the large amounts used in catalytic sulphuric acid works (*see* p. 322); in Italy £800 per kilo was paid in 1916 and £1600 to £2000 per kilo in 1917. A few kilos of platinum are also produced annually in Canada, the United States, and Australia (altogether about 50 to 60 kilos per annum).

The cost of refining platinum is to-day estimated at about £2 per kilo.

Two series of platinum compounds are known, *platinous* compounds of slightly basic character, in which platinum is divalent, and *platinic* compounds of acid character, which are more important and in which the platinum is tetravalent.

PLATINOUS CHLORIDE : $PtCl_2$. This compound is obtained on heating platinum sponge to 250° in presence of dry chlorine, or on heating chloroplatinic acid to 200° (*see below*). It forms a greenish-grey powder, insoluble in water and soluble in strong HCl. At a red heat it is converted into platinum and it forms soluble double salts with the chlorides of the alkali metals, such as $PtCl_2,2NaCl$; these may be considered as derivatives of **Chloroplatinous Acid, H_2PtCl_4.**

PLATINOUS CYANIDE : $Pt(CN)_2$. This compound has little importance in itself, but the double cyanides, which have a bright colour and strong and varied dichroism, are interesting. **Potassium Platinocyanide, $K_2PtCy_4,4H_2O$,** forms yellow rhombic prisms with a blue reflection. **Barium Platinocyanide, $BaPtCy_4,4H_2O$,** forms yellow monoclinic crystals which when viewed in various directions appear violet-blue or greenish-yellow, and are used for the production of screens which render *Röntgen-rays* visible.

PLATINIC CHLORIDE : $PtCl_4$ (Platinum Tetrachloride). This compound is obtained on heating platinum with aqua regia. On then evaporating in presence of excess of HCl, brownish-red deliquescent crystals of **Chloroplatinic Acid, $H_2PtCl_6 + 6H_2O$,** remain which are ordinarily called **Platinum Chloride.** It is a reagent which is used in chemical analysis, as it serves for the quantitative separation of K, NH_4, Cs, and Rb as yellow, crystalline precipitates which are almost insoluble in water and insoluble in alcohol, such as K_2PtCl_6, whilst the corresponding sodium salt is soluble in both water and alcohol. Chloroplatinic acid contains a complexion, $PtCl_6''$, and thus on electrolysing its aqueous solution, $PtCl_6$ separates at the anode. **Platinum Trichloride, $PtCl_3$,** is also known.

On treating a solution of H_2PtCl_6 with KOH and then with acetic acid, **Platinum Hydroxide, $Pt(OH)_4$,** separates. This compound is partly of basic and partly of acid character. Thus it is dissolved both by acids, excepting acetic acid, and by strong bases. The latter form salts corresponding with a hypothetical **Platinic Acid, $H_2Pt(OH)_6$.**

Numerous complex platinum compounds are known analogous to those of cobalt, which we have already studied (p. 846), and the platinammonium compounds are of special importance, such as **Platinodiammonium Chloride, $Pt(NH_3)_4Cl_2 . H_2O$,** known as *Magnus' Green Salt*, which is obtained from cold solutions of $PtCl_2$ by adding ammonia and then heating until the compound in question separates from the green solution, whilst **Platosemidiammonium Chloride, $Pt(NH_3)_2Cl_2$,** remains in solution.

The corresponding bromides, iodides, and nitrates are also known.

In 1909 L. Wöhler obtained and identified **Platinum Oxide, PtO_3,** with certainty.

PERIODIC SYSTEM OF THE ELEMENTS

If we take a comprehensive view of all the substances which we have studied, and which we have already divided into groups with respect to their valency, we shall now be able to find a reason for this classification, and we shall further be able to assemble certain regularities which unite the elements into individual groups and the groups with one another.

We have many times observed how certain laws which regulate matter refer rather to the molecules themselves individually than to the nature of the atoms or elements of which they are composed; such are the physical laws which regulate gases and which lead us among other things to the determination of molecular weights, and many laws which refer to solutions also depend exclusively on the number of ions and not on their nature. On the other hand, many properties of the elements are a function of their atomic weights, and thus we find that the specific gravity of the halogens, the alkali metals, and other groups of elements increases with increase of the atomic weight. The colour of these same halogens is a function of the atomic weight and its intensity varies from yellow to violet black with rise of the atomic weight from fluorine to iodine. The affinity of the halogens for hydrogen and for oxygen is also evidently a function of their atomic weight; we find the maximum affinity for hydrogen in the case of fluorine, whilst its affinity for iodine is least; on the other hand, the affinity for oxygen increases in the reverse direction.

Such regularities are found to a still greater extent in connection with the basic characters of the hydroxides of the alkali and alkaline earth metals and in their affinity for water, basicity, and general chemical activity, which increases in each individual group with increase of the atomic weight, and so on. Even if we ignore any atomic hypothesis on the nature of matter, these relations between weights and properties do not cease to exist, because that which we now call atomic weight is no other than the *simple weight* of each element, as it is called by Mendeléev, which enters as such or in a multiple quantity to form the molecules of simple or compound substances. That is a relative quantity which is exactly determined apart from any presupposed atomistic hypothesis by means of isomorphism, specific heat, etc.; it is also the quantity which we may derive from the combining weights deduced directly from analysis and which led Dalton to his law of multiple proportions. If we now collect all the elements in a given order or system regulated by the atomic weights of these elements themselves, we can include in a single comprehensive view the more important general laws regulating the relations which exist between the more marked physical and chemical properties of these elements and their grouping, and we can also predict the existence of new substances which have not yet been discovered. We can explain the reason for certain exceptions, for certain gaps, which are encountered in this harmonious and graduated grouping of the individual elements and groups, and we may also deduce new laws which permit us to attain a larger and wider horizon which will be gradually conquered through the continuous progress of science.

As early as 1817, and still further in 1829, Döbereiner divided the elements which presented the closest analogy with one another into *triads*, in each of which the differences of the atomic weights of the elements remained almost constant, such as Cl, Br, and I and Ca, Ba, Sr. In 1862 Chancourtois, and more especially Newlands in 1864, grouped all the elements into columns of increasing atomic weight and then divided them into several groups of 7 each, because after 7 elements the eighth differed greatly in its properties and resembled, on the other hand, the first of the previous group. The *law of octaves* was thus discovered. It was also found that the properties of each element of the preceding and succeeding groups which occupied the same progressive position and the elements which occupied, for example, the third position in each group were similar.

In 1859 Mendeléev and Lothar Meyer almost simultaneously discovered a complete system, according to which the various physical and chemical properties of all the elements were reduced to periodic functions of the atomic weight or atomic volume of the elements themselves, thus forming a natural grouping of the simple substances into several families or periods in which the analogy between the physical and chemical properties is periodically reproduced in each group of 7 elements (small period) up to chlorine (atomic weight 35·4); beyond this each period contains 17 elements, which may be arranged in two series, as is indicated in the Table on the following page, the atomic weights being given in round numbers. We have thus the *large periods* in which a progressive analogy is found in the first series of 7 elements, which are then followed by 3 elements (for example, Fe, Co, and Ni), similar to one another but differing from the first series, and separating it from the second series formed of 7 other elements. In the second large period the three intermediate elements are ruthenium, rhodium, and palladium. Then follows a period with many gaps due to still undiscovered elements and then a further large period which is somewhat incomplete, in which the three intermediate elements uniting Series 9 and 10 are represented by osmium, iridium, and platinum.

In the vertical columns the elements are found divided into other groups, each of which embraces elements which have the same valency in their hydrogen and halogen compounds or in their oxygen compounds, and thus from Groups I to Group VII the valency of the atoms with respect to oxygen increases from 1 to 7, whilst with respect to hydrogen it increases from 1 to 4 (from Na, K to C, Si, etc.), and then descends again to 1 in the case of fluorine. In the zero group (O) we find the 5 new gases discovered in the atmosphere which possess zero valency as they do not combine with any other substances. In Group VIII we find 3 triads of elements which, as we have seen, cannot be included in the other groups and which therefore together form a special group, in which we find so many analogies in the properties of the individual elements as fully to justify this division. Thus all have a very high melting-point and also a high specific gravity and consequently low atomic volume. Certain members behave as octavalent elements (OsO_4 and RuO_4) and form cyanides with complex ions.

On arranging the even series below Series 1 in such a manner that the odd series are displaced horizontally to the left, vertical columns result which contain various sub-groups of superposed elements which have more or less marked analogy with one another, such as K, Rb, Cs, and then Li, Na, Cu, Ag, Au, which all behave as monovalent elements. Then we have the two sub-groups (Ca, Sr, Ba) and (Gl, Mg, Zn, Cd, Hg) and again (Sc, Y, La, Yb) and (B, Al, Ga, In, Tl), etc.

Each series starts with the most electropositive (metallic) element and ends with the most electronegative (non-metallic) element; thus the vertical Column I includes the most positive metals and the vertical Column VII includes the most negative non-metals (halogens). In respect to their derivatives, we pass gradually in each horizontal series from the most basic compounds (alkali hydroxides) to the most acid compounds.

Various regularities are found on comparing the atomic weights of the elements of each series with the specific gravities and atomic volumes of the elements themselves or of their derivatives, such as the oxides, denoting in each case by "atomic volume" the number of cubic centimetres occupied by a gram-atom of the element in the solid or liquid state. This is obtained by dividing the atomic weight by the specific gravity. In Series 2 the specific gravity rises up to Al and then descends towards chlorine (liquid); on the other hand, the atomic volume diminishes from sodium to aluminium and then rises to liquid chlorine.

With the aid of the periodic system of the elements substances may be classified, although they themselves or their constituent elements have not been completely studied. Thus, for example, uncertainty formerly existed as to which formula was to be attributed to glucinum oxide—whether GlO or Gl_2O_3—and which atomic weight to assign to glucinum, because the volatile chloride was not then known and its molecular weight could not therefore be determined directly; on account of the analogies of glucinum with magnesium and aluminium, the selection of its atomic weight was not easy. The analysis of the oxide showed 9·4 parts of glucinum to 16 parts of oxygen, and if the formula GlO were attributed to the oxide, glucinum would have an atomic weight of 9·4, whilst if the oxide were Gl_2O_3, the atomic weight would be 14·1. On the other hand, glucinum oxide has somewhat marked basic properties, and thus approaches boron or to a still greater degree, lithium. With an atomic weight of 14·1 and an oxide, Gl_2O_3, the position of glucinum in the periodic system would be between oxygen and nitrogen, the oxides of which are of acid character, whilst if it had an atomic weight of 8·4 and an oxide, GlO, it would be found between lithium and boron, and, in fact, this is the position which may best be assigned to it. This position was later confirmed by the vapour density of glucinum chloride. It has been found possible to classify indium and other elements in the same manner, thus establishing or correcting their atomic weights with certainty.

The most exact experiments of recent years have always fully confirmed all deductions from the periodic system of the elements, and although it has been necessary to displace more than a few items of this grouping (*see* Table, p. 857), and although the periodic system may not always be in harmony with all the laws of modern chemistry, its positive basis remains assured, and will some day find a rigorous mathematical explanation. In the same way that the discovery of the planet Neptune was prophesied by Leverrier at Paris in 1846 and by Adams in England, by mathematical calculations, thus constituting an astronomical triumph, the discoveries of scandium, gallium, and germanium in recent years were not less surprising and marvellous. In 1869 Mendeléev, by studying the gaps which remained unfilled in his classification, had established that in the third series, below boron, and at the side of titanium, there should be found an element which he called *ekaboron*, and which was later actually discovered and called scandium. In the fourth series, corresponding with aluminium and silicon there should have been *eka-aluminium* of atomic weight 69 and *ekasilicon* of atomic weight 73; in 1875 Lecoq de Boisbaudran actually discovered gallium of atomic weight 70, corresponding with eka-aluminium, and in 1866 C. Winkler discovered germanium of atomic weight 72·5, which corresponded with the ekasilicon of Mendeléev. The correspondence of the properties of germanium with those of ekasilicon, described in advance by the founder of the periodic system in 1871, was still more surprising. Mendeléev had assigned to

PERIODIC SYSTEM OF THE ELEMENTS

Group and Valency		O	I	II	III	IV	V	VI	VII	VIII		
Type of the hydrogen or halogen compounds (X = halogen or H) (M = element)		—	MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX	—	—	—
Type of the oxygen compounds		—	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4	MO_2	MO
Period	Series											
I	1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	—	—	—
II	2	Ne 20	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·4	—	—	—
III	3	A 39·9	K 39·2	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Ni 59	Co 59
	4	—	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80	—	—	—
IV	5	Kr 82	Rb 85	Sr 87	Y 89	Zr 90	Cb 94	Mo 96	—	Ru 102	Rh 103	Pd 106
	6	—	Ag 108	Cd 112	In 114	Sn 118	Sb 120	Te 127·6	I 126·5	—	—	—
V	7	X 128	Cs 133	Ba 137	La 138	Ce 140	(Pr 140) (Nd 144)	—	Sa 150	—	—	—
	8	—	—	—	—	—	—	—	—	—	—	—
VI	9	—	—	—	Yb 173	—	Ta 183	W 184	—	Os 191	Ir 193	Pt 195
	10	—	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—	—	—	—
	11	—	—	—	—	Th 232	—	U 239	—	—	—	—

ekasilicon a specific gravity of 5·5 and an atomic volume of 13; to the corresponding oxide he assigned a specific gravity of 4·7 and to the chloride a specific gravity of 1·7. Fifteen years later C. Winkler found the specific gravity of germanium to be 5·47, its atomic volume to be 13·1, the specific gravity of the oxide to be 4·603 and that of the chloride to be 1·887. As will be seen, the prophecy was fulfilled with mathematical accuracy.

The periodic system, by indicating the intimate connection between the atomic weights and other properties of the elements, thus showing that the properties are a function of the atomic weights, became a most important contribution to the hypothesis of the *unity of matter* (p. 124), a hypothesis which represents the most advanced side of that to which the powers of the greatest geniuses are directed. The discoveries made by means of the spectroscope and of radio-active substances (p. 124) have again accentuated and justified these hopes, and perhaps in the near future the hopes of to-day will be realised, and be the prelude to a new era of progress and of conquest in theoretical and practical fields.

INDEX

Aalborg cement kilns, 759
Abrasives, 500
Absorption, Coefficient of gas, 74
Accumulators, 518, 525
Acid eggs, 302
Acids, 96, 274
  Nomenclature of, 275
Actinium, 126, 128, 131
Adiabatic change, 54
Affinity, Chemical, 48, 72
Agate, 497, 501
Air, Atmospheric, 334
  Drying of, 264
  Fixed, 16
  gas, 365, 489, 490
  Inflammable, 133
  Liquid, *see* Liquid air
  Phlogisticated, 332
  Vital, 17, 188
Alabaster, 619, 626
  Gypseous, 626
Albite, 737
Alchemy, 13
Alcoholometry, 78
Aldebaranium, 775
Algæ, Iron, 247
  Marine, 163
Algaroth, Powder of, 430
Alite, 751
Allotropy, 124, 202, 206, 435, 511
Alloys, 513
  Aluminium, 726
  Chemical behaviour of, 517
  Coefficient of elasticity of, 517
  Copper, 699
  Electrical conductivity of, 515
  Fusible, 792
  Melting-point diagram of, 517
  Micrography of, 517, 828
  Pyrophoric, 189
  Theory of the melting-point of, 792
Alum, Burnt, 737
  Potash, 736
  Roman, 736
Alumina, 731
  Hydrated, 387
Aluminates, 733
Aluminite, 736
Aluminium, 723
  acetate, 733
  alloys, 726
  amalgam, 726
  brass, 727
  bronze, 725, 726
  chloride, 734
  fluoride, 734
  hydroxide, 732
  lakes, 733
  lamp, 726
  nitride, 735
Aluminium oxide, 731
  Properties of, 726
  silicate, 737
  Statistics of, 730
  sulphate, 735
Alumite, 529, 736
Alumino-thermic welding, 727
Alums, 736
Alundum, 732
Amalgam, 517
  Aluminium, 726
  Tin, 778
Amalgamation, 718
Ambligonite, 607
Amethyst, 497
Amicroscopic particles, 107
Amidol, 714
Aminophosphoric acid, 418
Aminosulphonic acid, 330
Ammonia, 353
  Analytical tests, 375
  Aqueous, 360
  Chemical properties, 355
  from lighting gas, 356
  from nitrogen and hydrogen, 372
  from peat, 361–6
  Industrial preparation, 355
  Liquid (anhydrous), 375
  Physical properties, 354
  Specific gravity of aqueous, 354
  Statistics, 375
  Synthetic, 366
Ammonium, 355, 608
  compounds, 608–14
  dichromate, 798
  ferrosoferrocyanide, 842
  magnesium arsenate, 426
  metal, 608
  metavanadate, 434
  molybdate, 799
  nickel sulphate, 846
  persulphate, 588, 612
  platinichloride, 852
  thiocyanate, 841
  trithiocarbonate, 548
Ampere, International, 519
Amphibole, 668
Amphoteric reaction, 603
Analysis, 45
  Volumetric, 99
Anatase, 502, 503
Anglesite, 782
Anhydrite, 626
Animal charcoal, 404, 457, 648
  oil, 361, 404
Anions, 95
Anisotropic liquids, 117
Anisotropy, 117
Annular furnace, 744
Anoxæmia, 485

Ansell's apparatus, 471
Anthracite, 450
Antichlor, 584
Anti-friction metal, 428, 517, 833
Antimonates, 431
Antimonic acid, 431
    anhydride, 431
Antimonite, 426
Antimonium crudum, 428, 432
Antimony, 426
    alloys, 428
    blende, 427
    Butter of, 430
    Cinnabar of, 428, 432
    Explosive, 429
    Flowers of, 431
    Golden sulphide of, 432
    Halogen compounds of, 430
    Hydrogen compounds of, 430
    hydroxide, 431
    Liver of, 433
    oxychloride, 430
    Oxygen compounds of, 430
    pigments, 428
    Refining of, 427
    salt, 430
    sulphides, 432
Antimonyl hydroxide, 431
Antiozone, 205
Apatite, 402, 647
Aqua regia, 401
Aqueduct, Apulian, 233
Aqueducts, 233
Aquo salts, 849
Aragonite, 618, 663
Arc, Electric, 465
    Speaking, 221
Arenolite, 745
Argentan, 700, 844
Argentite, 707
Argon, 351
Argyrodite, 775
Arsenates, 426
Arsenic, 418
    acid, 425
    anhydride, 425
    compounds, 420–6
    mirror, 420
    Vitreous, 423
Arsenious acid, 425
    anhydride, 423
Arsenites, 425
Arsenolite, 423
Asbestos, 668
    Platinised, 321, 853
Asbolite, 846
Atmosphere, 334
    Composition, 335
    Height, 134, 336
    Moisture, 337
    New gases of the, 351
    Origin, 134
    Pressure, 336
Atomic heat, 112
    heat of combination, 114
    theory, 22
    volume, 511
    weights, 44, 112
        Determination of, 88, 124
        Table of, 43
Atomisers, 790
Atoms, 32
    Vortex, 123
Auer gas mantles, 505, 506
Auric acid, 722
    compounds, 722
Aurous compounds, 722
Austenite, 830
Avogadro's hypothesis, 33
    law, 32
Azoimide, 376
    iodide, 377
Azurite, 691, 703

Bacteria, Ærobic, 249
    Anærobic, 249
    beds, 251
    Denitrifying, 334
    Nitrogen, 349
    Nitrifying, 350
Bacterium subtilis, 236
Balloons, Experimental, 336
Barium, 663
    chromate, 798
    cyanamide, 368
    platinocyanide, 854
    salts, 663–7
Barytes, 666
Bases, 96, 274
    Dissociation of, 98
    Nomenclature of, 275
    Poly-acid, 274
    Polyhydric, 274
Bastian lamp, 687
Bauxite, 723, 730, 731
Beckmann's apparatus, 87
Belite, 751
Beryl, 675
Beryllium, *see* Glucinum
Betaine, 356
Bicarbonates, 475
Birkeland-Eyde process, 391
Bismuth, 792
    Fusible alloys of, 792
    Magister of, 794
    salts, 793
Bismuthic acid, 793
Bismuthine, 792, 794
Bitter salt, 672
Black ash, 593
Blankite, 588
Blast furnace, 812
    gases, 814
Bleaching powder, 622
Blende, 675, 683
    burners, 295
    Pitch, 803
Blood as fertiliser, 644
Blue, Prussian, 842
    Thénard's, 847
    Turnbull's, 843
Boiler incrustations, 241, 619
Boiling-point, 86
Bomb, Asphyxiating, 493
    Berthelot's, 62
    Calorimetric, 461
Bone, 647
    ash, 404, 647
    black, 404, 457
    flour, 647
    powder, 647
    superphosphate, 647
Boracite, 506
Borax, 510, 604
Bordeaux mixture, 705
Boric acid, 507, 509
    anhydride, 507
Borocalcite, 506

Boron, 506
  compounds, 507
  hydride, 136, 507
  nitride, 367, 510
Boronatrocalcite, 604
Bradolytes, 97
Brass, 699
  Aluminium, 727
Braunite, 804
Bricks, 742, 743
  Artificial, 745
Brine for refrigerating machines, 621
Briquettes, 459
Britannia metal, 428
Brody's reaction, 438
Bromates, 187
Bromine, 158
  water, 158
Bronze, 699
  Aluminium, 725, 726
  Tungsten, 802
Brookite, 502, 503
Brownian movement, 107
Bunsen cell, 526
Bunsenite, 846
Butter of antimony, 430
  of tin, 780
  of zinc, 682

Cacodyl, 421
Cadmium, 684
  salts, 684
Cæsium, 551
Caffaro paste, 705
Calamine, 675
Calcite, 618
Calcium, 614
  bicarbonate, 619
  bisulphite, 281, 626
  bromide, 622
  carbide, 638
    Analysis, 642
    furnaces, 638
    Statistics, 641
  carbonate, 618
  chloride, 620
  cyanamide, 368–72
  ferrocyanide, 841, 843
  fluoride, 622
  hydride, 615
  hydrosulphide, 626
  hydroxide, 617
  hypochlorite, 622
  iodide, 622
  monophosphate, 281
  nitrate, 392, 625
    Basic, 392, 625
  nitride, 615
  nitrite, 625
  oxide, (*see* also Lime) 615
  peroxide, 618
  phosphates, 643
  plumbate, 787
  pyrophosphate, 643, 658
  silicate, 628
  silicide, 499
  sulphate, 626
  sulphide, 625
  sulphite, 626
  superphosphate, Ammoniacal, 658
  tungstate, 803
Calcspar, 618
Caliche, 575
Calomel, 688
Calorie, 51, 111
  Large, 61
  Rational, 61
  Small, 51, 61
Calorific power, 461
  Molecular, 460
Calorimeter, Berthelot-Mahler, 461
  Lewis Thompson, 461
Capillarity, 79
  of solutions, 82
Caput mortuum, 838
Carat, 437
Carbofrax, 500
Carbon, 435
  Allotropic forms, 435
  Amorphous, 435
  compounds, 469
  dioxide, 471
    Analysis of, 484
    Applications, 482
    Liquid, 481
    Preparation, 475
    Properties, 471
    Solid, 482
    Statistics, 483
    Thermochemistry of liquid, 481
  disulphide, 493
  Electrode, 440
  Gas, 458
  group, 435
  Halogen compounds, 470
  "Metallic," 458
  monosulphide, 496
  monoxide, 484
    Calorific value, 460
  oxychloride, 492
  oxysulphide, 496
  Retort, 458
  silicide, 499
  suboxide, 492
  tetrachloride, 470
  tetra-iodide, 471
Carbonado, 436
Carbonic acid, 471, 474
Carbonyl, 492
  chloride, 492
  nitride, 493
Carborundum, 440, 499
Carnallite, 149, 530, 531, 532, 535, 669
Carnotite, 129
Carnot's cycle, 54, 55
  principle, 54
Caro's acid, 329
  reagent, 588
Cassiopœium, 775
Cassiterite, 776, 780
Cast-iron, 811, 812
  Classification, 819
  Density of, 818
  Grey, 811, 818
  Malleable, 818
  Special, 818
  Statistics, 831
  Tempering of, 818
  White, 811, 818
Catachromy, 717
Catalases, 70, 110
Catalysis, 66, 70, 107
Catalysts, 66, 71, 318, 321, 715
  Negative, 71, 583
  Poisons for, 374
  Specific, 72
Catatype, 715, 716
Cation, 94

Cation, Polyvalent, 108
Celestine, 662
Celite, 751
Cellarius apparatus, 176
Cells, Irreversible, 526
  Reversible, 525
Cement, 747
  Blast furnace slag, 764
  Burnt, 763
  Coefficient of expansion, 768
  Composition of, 753
  Dead, 752
  English, 628
  Fineness of, 764
  Grappier, 763
  Grinding of burnt, 763
  Hydraulic index, 752
  kilns, 758–63
  Magnesia, 672
  manufacture, 753
  Natural, 748
  Portland, 749
    Artificial, 751
    Density, 764
    White, 764
  Production, 769
  Raw materials, 752
    Grinding of, 754
  resistant to sea-water, 764
  Roman, 749
  Setting of, 110
  Slag, 763
  Slow- and rapid-setting, 752
  Sorel, 672
  Statistics, 768
  Testing, 764
  Theory of setting and hardening, 751
  Time of setting, 765
  Uses, 768
Cementation iron, 821
Cementite, 820, 828, 830
Ceramics, 737
Cerite, 125, 773
Cerium, 773
  salts, 774
Cermak-Spirek (mercury) furnaces, 685
Cerussite, 782
Cervantite, 426, 431
Chalcedony, 501
Chalcopyrite, 691
Chalcosine, 691, 702
Chalk, 618, 743
  Phosphatic, 647
  Tailors', 674
Chameleon, Mineral, 807
Chamotte, 739
Charcoal, Animal, 457
  Bone, 404
  Peat, 445
  Wood, 457
Chemical phenomena, 3
Chlamydothrix, 247
Chlorates, 186
Chlorhydrin, 330
Chloric acid, 186
Chlorine, 149
  Analysis, 158
  Applications, 151
  Catalytic, 154
  Deacon-Hurter process, 155
  Dunlop process, 154
  Electrolytic, 556
  Electrolytic preparation, 156
  hydrate, 150
Chlorine, Liquid, 151, 157
  oxides, 184
  Preparation of, 152
  Statistics, 151
  water, 150
  Weldon process, 154
  Weldon-Pechiney process, 156
Chloroauric acid, 723
Chlorophosphoric amide, 418
Chlorophyll, 473
Chloroplatinic acid, 854
Chloroplatinous acid, 854
Chlorostannic acid, 781
Chlorosulphonic acid, 330
Chlorous acid, 184
Chromates and dichromates, 796
Chrome alum, 795, 797, 799
  green, 795
  iron ore, 794
  yellow, 798
Chromic acid derivatives, 795
  anhydride, 796
  chloride, 795
  fluoride, 795
  hydroxide, 795
  oxide, 795
  sulphate, 795
Chromium, 794
  oxychloride, 798
  Recovery of, 797
  trioxide, 796
Chromous chloride, 795
  hydroxide, 795
  sulphide, 795
Chromyl chloride, 798
Chrysoberyl, 675
Chrysotile, 668
Cinnabar, 685, 691
  of antimony, 432
Clapeyron's equation, 55
Claudetite, 423
Clay, 724, 737
  Ceramic, 743
  for bricks, 743
  Foundry, 740
Clinker, 759, 763
Coal, 447–51
  Agglomerated, 459
  as a source of heat, 460
  Boghead, 448
  Brown, 446
  Cannel, 448
  Composition, 442
  Origin, 442
  Reserves of, 450
  Spontaneous ignition, 442, 448
  Statistics, 449
Cobalt, 846
  alums, 848
  aquo-salts, 849
  enamels, 847
  salts, 847–850
Cobaltine, 846
Cobaltipotassium nitrite, 848
Cockerill engines, 814
Coke, 451
  Metallurgical, 455
  Peat, 444, 445
Coke-ovens, 451
Colcothar, 317, 838
Colemanite, 506, 604
Collargol, 109
Colloidal solution, 105
  of platinum, 853

Colloids, 106
  Irreversible, 109
  Protective, 109
Columbic acid, 434
Columbite, 434
Columbium, 434
Combining weights, 19, 48
Combustible and supporter of combustion, 151
Combustion, 189
  Flameless or surface, 464
  Heat of, 461
Compressed or liquefied gases, 138, 157, 192, 278, 375, 480, 481
  Cylinders for, 192, 278, 481, 833
Compressors for CO_2, 480
Concentration in vacuo, 562, 567
  product, 706
Concrete, 768
  Reinforced, 768
Condensed system, 119
Conductivity, Electrical, 512
  Equivalent, 102
  Specific, 102
Conductors, Electric, 95
Cones, Seger, 738
Conservation of energy, 4
  of mass, 8, 9
Continuous fusion (carbide) furnace, 640
Converter, Bessemer, 820, 821
  Holway-Manhes, 695
Co-ordination number, 848
Copper (*see also* Cupric *and* Cuprous), 691
  alloys, 699
  Applications, 699
  arsenate, 706
  arsenite, 706
  Basic carbonate, 703
  Black, 695
  Cementation, 697
  compounds, General reactions of, 707
  Electrolytic, 697
  Extraction, 692–9
    American process, 695
    Chlorination process, 697
    Dry method, 692
    Electrolytic, 697
    Wet method, 696
  ferrocyanide membranes, 80
  hydroxyammoniate, 699
  hydroxychloride, 702
  iodide, 702
  nitrate, 703
  ores, 691
  Properties, 699
  Refining, 696
  thiocyanate, 841
Coprolite, 402
Corrosive sublimate, 689
Corundum, 723, 731
Coulomb, 519
Covering powers of pigments, 788
Crenothrix, 247
Critical point, 29
Croceocobalt salts, 848
Crocoite, 782, 794
Crown glass, 629
Cryohydrate point, 122, 259
Cryohydric mixtures, 122
Cryolite, 724, 734
Cryoscopic anomalies, 90
  apparatus, 89
Cryoscopy, 89
Crystalline substances, 115
Crystallography, 115
Crystalloids, 106
Crystals, Lead chamber, 381
  Liquid, 117
  Living, 117
  Mixed, 116
  Soft or Plastic, 117
Crystoballite, 630
Cupel furnace, 707
Cupola furnaces, 693, 818
Cupric bromide, 703
  chloride, 703
  hydroxide, 702
  oxide, 702
  sulphate, 703
    Uses and statistics, 705
  sulphide, 705
Cuprite, 691, 702
Cuproscheelite, 799
Cuprous bromide, 702
  chloride, 702
  cyanide, 702
  hydride, 702
  hydroxide, 702
  oxide, 702
  sulphide, 702
Curcuma rubricaulis, 83
Cyanamide, 369, 372
Cyanogen compounds, 496
Cylinders for compressed gases, 192, 278, 481, 833

Daguerrotype, 713
Dana tubes, 756
Daniell cell, 521
Danks rotary (puddling) furnace, 819
Davy safety lamp, 464
Dead Sea, 228
Decroline, 588
Deflocculation, 440
Deforestation, 223
Delta metal, 699
Density of gases, 34
  liquids, 75
  vapours, 34
Descloizite, 433
Detonating mixture, 136, 190
Devitrification, 631
Dialyser, 106
Diamagnetism, 58
Diaminophosphoric acid, 418
Diaminopyrophosphoric acid, 414
Diamond, 436
  Artificial, 437
Diaspore, 723, 732
Dicyandiamide, 369, 371, 548
Dicyandiamidine, 372
Didymium, 775
Dielectric constant, 95
Dieline, 470
Dietzsch stage (cement) kilns, 758
Diffusion of gases, 40
Dihydroxytetramminoplatinum sulphate, 849
Dimercuroammonium chloride, 688
Dinas bricks, 739
Dippel animal oil, 404
Dissociation, Degree of, 102, 379
  Electrolytic, 94, 705
  Heat of, 332, 487
  Hydrolytic, 102, 271
  Ionic, 271
  of vapours, 40
Disulphaminic acid, 331
Disulphuric acid, 274, 284
Disulphurous acid, 274

Dithionic acid, 274, 329
Divariant system, 121, 208
Döbereiner lamp, 137
Dolomite, 475, 668, 673
Donath's reaction, 446
Doppioni for sulphur extraction, 216
Double decomposition of salts, 97
Dowson gas, 365, 490
Drummond light, 137, 190
Dualistic formulæ, 45
Ducco pyrites burners, 295
Ductility, 511
Dyne, 27, 61
Dysprosium, 502

Earthenware, 741
Ebullioscopy, 86
    Anomalous, 90
    Beckmann's apparatus for, 87
Efflorescence, 581
Effusiometer, Bunsen's, 40
Eggs, Preservation of, 258
Eka-aluminium, 772, 857
Ekaboron, 773, 857
Ekasilicon, 775, 857
Electric (aluminium) furnaces, 724
    (carbide) furnaces, 638
    induction (carbide) furnaces, 638
    lamps, 801, 802
    (steel) furnaces, 824
Electrochemistry, 518
Electrodes, 639
Electrolysis, 523
Electrolytes, 94, 523
    Strong and weak, 103
Electrolytic dissociation, 94, 705
Electrons, 105, 131
    Magnitude of, 127
Electro-plating, 844
Elevators, Acid, 302
Emanation, Radium, 126
Emerald, 675
Emery, 500, 723, 731
Emulsoids, 106
Enamels, 743
Enantiotropic substances, 208
Energy, 1, 127
    Chemical, 1, 6, 60
    Conservation of, 4
    Degradation of, 7, 26, 55
    Electrical, 6
    Free, 8, 72
    Hydraulic, 518
    Indestructibility of, 7
    Internal, 53
    Kinetic, 4
    Luminous, 6
    Mechanical, 4
    of combination, 72
    of distance, 1
    of volume, 27
    Potential, 4
    Sound, 6
    Thermal, 5, 6
    transformations, 6
Entropy, 72
Epsom salts, 672
Equations, Chemical, 59
    Thermochemical, 60
Equilibrium, 64, 372, 382, 394
    Complete, 121, 208
    Factors of, 66
    Heterogeneous, 66
    Homogenous, 66
Equilibrium, Incomplete, 119, 121, 208
    in heterogeneous systems, 118
    Ionic, 103
    Isothermal, 68
    Metastable, 73
    Mobile, 64, 66
Equivalent, Chemical, 21, 48
    Electrochemical, 520
    Electrothermal, 520
    of heat, Mechanical, 7, 51, 61, 225
Erbium, 773
Erg, 27, 51, 61
Eternite, 669
Ether, Cosmic, 5, 123
Europium, 502
Eutectic alloys, 514
    point, 257, 516
        of iron, 829
Evaporation, Heat of, 226
Exothermic reactions, 370
External work, Theory of, 341

Felite, 751
Felspar, 528, 529, 724, 737, 740
Ferberite, 799
Ferments, Inorganic, 110
Ferric acid, 840
    chloride, 838
    hydroxide, 838
    nitroprussiate, 837
    oxide, 838
    phosphate, 839
    sulphate, 839
    sulphide, 839
Ferricyanides, 840
Ferrite, 820, 829
Ferro-cement, 764
Ferrocyanides, 842
Ferrohydrochloric acid, 837
Ferromanganese, 827, 828
Ferromolybdenum, 828
Ferrosilicon, 497, 827, 828
Ferroso-ferric bromide, 537
    iodide, 537
    oxide, 838
Ferrosulphuric acid, 837
Ferrotitanium, 503
Ferrous bicarbonate, 837
    carbonate, 837
    chloride, 836
    nitroprussiate, 837
    oxide, 836
    phosphate, 837
    sulphate, 836
    sulphide, 837
    titanate, 503
Ferrovanadium, 828
Ferrugine, 839
Fertilisers, Chemical, 643
    Nitrogenous, 347, 644
    Phosphatic, 645
    Potash, 529
Fertilising, Theory of, 350
Fire grates, 462
Firebricks, 739
Firedamp, 190
Fixing agents, Photographic, 715
Flame, Nature of, 464
    Oxy-hydrogen, 137
    Temperature of, 465
Flavocobalt salts, 848
Flint, 501
    glass, 629
Florida earth, 738

Flue gases, Analysis of, 463
Fluorescence, 125
Fluorine, 147
Fluorite, 622
Fluorspar, 622
Fluxes, 693, 741, 812
Formulæ, Alchemistic, 42
    Chemical, 42, 44
    Constitutional, 49
    Dualistic, 45
    Empirical, 49
    General gas, 26
Franklinite, 804
Freedom, Degrees of, 118
Freezing mixtures, 257
    point, 88
        Depression of, 88
Frigorie, 259
Frühling-Michælis (cement-testing) balance, 766
Fucus, 163
Fuels, 441
    Briquetted, 459
    Calorific value of, 461
Fuller's earth, 674, 738
Fumaroles, 507
Fusel oil, 458

Gadolinite, 775
Gadolinium, 502
Gaillard tower, 309
Galena, 782, 791
Galera sulphur furnace, 216
Gallionella, 247
Gallium, 772
Galvanoplastics, 844
Garnierite, 844
Gas, Expansion with external work, 346
    for gas engines, 490
    General equation, 26
    isotherms, 28
Gas producer, Delwik-Fleischer, 488
    Golia, 491
    Mond, 363, 365
    Siemens, 634
    Water, 487
Gases, Optical properties, 55
    Solubility in liquids, 73
        salt solutions, 74
Gay-Lussac tower, 300
Gaylussite, 554
Gel, 106
Gelatinisation, 106
Geocoronium, 134
German silver, 700
Germanium, 775
Gill regenerative sulphur furnace, 215
Ginisi, 214
Giobertite, 613, 670, 673
Glaserite, 546
Glass, 628
    Composition of, 631
    Crystal, 629
    Expansion of, 631
    furnaces, 634
    Hardened, 636
    Normal, 631
    Quartz, 630
    Raw materials for making, 632
    Refractive index of, 632
    Soluble potash, 547
    Soluble soda, 606
    Statistics, 637
Glauberite, 580
Glauber's salt, 580
Glaze, 743
Glover tower, 303
Glucinum, 668, 675
    salts, 675
Gneiss, 501
Gold, 717
    Amalgamation, 718
    Applications, 721
    chlorides, 722
    coinage, 721
    Colloidal, 108, 109, 721
    compounds, 722
    Extraction, 718
        Chlorine process, 719
        Electro-chemical process, 719
        Forrest process, 719
    Fineness of, 721
    hydrosol, 108, 109
    iodide, 722
    Mosaic, 781
    number, 109
    oxides, 722
    Properties, 720
    Refining, 720
    salts, 722
    Statistics, 721
    sulphides, 722, 723
Goutal's formula, 461
Gradation (of salt solutions), 568
Gram-molecule, 26
Granite, 501
Graphite, 438, 830
    Acheson, 440
    Artificial, 440
    crucibles, 438
    for lubricants, 439
Graphitic acid, 438
Graphitites, 439
Graphititic acid, 439
Grappier cement, 763
Greek fire, 407, 495
Green, Chrome, 795
    Cobalt, 682
    Guignet's, 795
    Paris, 424
    Rimmann's, 682
    Scheele's, 424, 707
    Schweinfurth, 424
    Swedish, 707
    Zinc, 682
Grinding-wheels, 500
Gritti's sulphur apparatus, 216
Guano, 646
Guareschi's reaction, 159
Gunpowder, 542
Gutzeit's reaction, 420
Gypsum, 282, 626
    Alumed, 628
    Burnt, 627
    Dead or overburnt, 627
    Fibrous, 626
    for paving, 627
    Ordinary, 628
    Setting of, 627

Hæmatite, 809, 838
Halogens, 147
    Compounds with one another, 184
    Hydrogen compounds, 166
    Oxygen compounds, 184
Hasenclever's apparatus (chloride of lime), 623
Hauerite, 804
Hausmannite, 804, 806

- Hay, Heating of moist, 190
- Heat insulators, 259, 463
    - Radiation of, 464
- Heavy spar, 663, 666
- Helbig (nitrogen) furnace, 397
- Helianite, 310, 400, 819
- Helium, 135, 352
- Hermite apparatus (hypochlorites), 573
- Héroult (steel) furnace, 824
- Hexamminocobalt salts, 848
- History of Chemistry, 9
- Hofmann annular (brick) kiln, 744
- Hofmann's vapour density apparatus, 35
- Holmium, 502
- Homeomeria, 12
- Homogeneous and heterogeneous systems, 118
- Horn powder, 644
- Horse power, 62
    - Electric, 62, 492
    - hour, 460
    - Steam, 492, 520
- Hübnerite, 799
- Hydrargillite, 723, 732
- Hydrates, Heat of formation of, 530
- Hydrazine, 376, 668
- Hydrazoic acid, 376
- Hydrides, 136
- Hydriodic acid, 182
- Hydrobromic acid, 181
- Hydrochloric acid, 169, 387
    - Analysis, 181
    - Anhydrous liquid, 170
    - Industrial manufacture, 173
    - Laboratory preparation, 172
    - Legislation concerning, 175
    - Properties, 170
    - Purification, 179
    - Specific Gravity table, 180
    - Statistics, 171
    - Synthetic, 179
    - Testing, 181
    - Thermochemistry of formation, 177
    - Uses, 170
- Hydrocyanic acid, 497
- Hydrofluoric acid, 167
- Hydrofluosilicic acid, 499, 656
- Hydrofluotitanic acid, 503
- Hydrogel, 107
- Hydrogen, 133
    - Active, 135
    - Analysis, 146
    - antimonide, 430
    - arsenide, 420
        - Antidote for, 420
        - Solid, 421
    - Ascensional power, 137
    - boride, 507
    - Cathodic, 135
    - Chemical properties, 135
    - Industrial preparation, 141
    - Laboratory preparation, 139
    - Liquid, 135
    - Metallic, 135
    - peroxide, 266, 735
        - Concentration of, 269
        - Solid, 270
    - persulphide, 273
    - phosphide, 410
        - Liquid, 411
        - Solid, 412
    - Physical properties, 134
    - Purification, 141
    - selenide, 273
    - silicide, 498
- Hydrogen, Statistics, 138
    - sulphide, 270
        - Preparation, 272
    - telluride, 273
    - Uses, 136
- Hydrolysis, 97, 108, 271
- Hydrometer, Beaumé, 78
    - Beck, 78
    - Cartier, 79
    - Gay-Lussac, 78
    - Tralles, 78
    - Twaddel, 79
- Hydrometers, 77
- Hydronium hypothesis, 91
- Hydrosols, 106, 107
- Hydrosulphite formaldehyde compounds, 587
- Hydrosulphites, 282, 586
- Hydrosulphurous acid, 274, 282, 586
- Hydroxydimercuroammonium hydroxide, 689
- Hydroxylamine, 376
- Hygrometer, 337
- Hyperol, 270
- Hypochloric acid, 185
- Hypochlorites, 185
- Hypochlorous acid, 184
    - anhydride, 184
- Hyponitrous acid, 378
- Hypophosphates, 413
- Hypophosphites, 413
- Hypophosphoric acid, 413, 417
- Hypophosphorous acid, 413, 414
- Hyposulphites, 282
- Hyposulphuric acid, 274, 329
- Hypothiophosphites, 408
- Hyraldite, 588

- Iatrochemistry, 14
- Ice, 224, 258
    - Analysis of, 260
    - Artificial, 259
    - machines, 259
        - using ammonia, 260
        - carbon dioxide, 264
        - dry air, 262
        - sulphur dioxide, 263
    - Natural, 258
    - Uses and statistics, 264
- Iceland spar, 618
- Imino group, 331
- Iminosulphonic acid, 331
- Incandescent gas lighting, 505
- Indicators, 100
- Indium, 772
- Ingots, 823
- Ink, Sympathetic, 847
- Insulators, Thermal, 259, 463
- Invar, 844
- Iodates, 187
- Iodine, 161
    - Analysis of, 165
    - bromide, chloride, fluoride, 184
    - Tincture of, 161
- Iodothyrin, 162
- Ionic theory, 94
- Ionisation, 128, 706, 733
    - of gases, 128
- Ionium, 130
- Ions, 57, 94, 105
    - Actual and potential, 100, 101
    - Analytical tests for, 98
    - Colour of, 104
    - Concentration of, 103, 542
    - Equilibrium of, 103
    - Heat of formation of, 101

Ions, Mobility of, 103
  Theory of, 94
  Transport numbers of, 103
  Valency of, 99
Iridium, 852
Iron(*see* also Steel), 809
  carbide, 830
  carbonyls, 492
  Cast (*see* Cast-iron)
  Chemically pure, 810
  chromite, 795
  Classification of kinds of, 811
  cyanides, 840
  Electrolytic, 820
  Magnetic oxide, 838
  Metallurgy of, 811
  Meteoric, 810
  Micrography of, 809, 828
  Natural, 809
  Neutral, 811
  ores, 809
    Production, 835
  Preservation from rusting, 810
  Properties of, 810
  Puddling of, 813, 819
  pyrites, 217, 810, 839
  sesquioxide, 838
  Soft, 811, 819
  Statistics, 834
  vitriol, 836
  Wrought-, 819
Isodimorphism, 116
Isohydrism, 103
Isomerism of hydration, 849
Isomorphism, 115
Isotachyol, 236
Isothermal change, 54
  curves, 25, 28
Isotonic solutions, 83

Javel, Eau de, 537, 573
Jonkite, 609
Joule, 61

Kainit, 530, 532, 543, 672
Kalkstickstoff, 371
Kaolin, 723, 737, 745
Kelp, 163
Kelvin degrees (temperature), 113
Kermes, Mineral, 432
Kieselguhr, 463
Kieserite, 543, 669, 672
Kilogram-metre, 61
Kilojoule, 62, 520
Kilowatt, 62
Kindler (CO_2) furnaces, 476
Kinetic theory of gases, 37
Kipp's apparatus, 139
Knebelite, 804
Körting's apparatus (drying), 657
Kominor, 754
Kröhnke filter, 237, 248
Krypton, 353
Kühlmann emulsifier, 217

Labarraque, Eau de, 573
Lagoni, 508
Lakes, 733
Laming mixture, 143
Lamp-black, 458
Lanthanite, 774
Lanthanum, 506, 774
Lapis lazuli, 770
Lardarellite, 506
Latent heat, 23
Laughing gas, 378
Law, Boyle and Marriotte's, 23
  Dulong and Petit's, 112
  Faraday's, 519, 522
  Gay-Lussac and Dalton's, 25
  General gas, 26
  Henry's, 73
  Hess's, 62, 63
  Le Chatelier's, 64, 257
  Mass, 68, 103, 320
  Melting-point, 792
  of conservation of energy, 4
  of conservation of mass, 8
  of constancy of the sum of the heats, 63
  of constant proportions, 21
  of gradual reactions, 73
  of isothermal equilibrium, 68
  of multiple proportions, 21, 22
  of octaves, 855
  of phases, 118, 208
  of reaction, 64
Laws of thermochemistry, 60
  of thermodynamics, 7, 51
Lead, 782–92
  chambers (*see* Sulphuric acid)
  compounds, 785–92
  Extraction, 782
  Hard, 284, 428
  poisoning, 788
  Properties, 783
  Pyrophoric, 189, 783
  Refining, 783
  Statistics, 784
  sulphide, 271, 791
  White, 788
Le Chatelier's principle, 64
Leclanché cell, 526
Lepidolite, 551, 607
Leucite, 529, 737
Lignin, Reaction for, 446
Lignite, 446
Lignolite, 672
Lime, 615
  Chloride of, 622
  Determination in cement, 768
  Hydraulic, 748
  kilns, 616
  Quick, 615
  Slaked, 617
  Soda, 618
  Uses, 617
  water, 242
Limelight, 137
Limonite, 809, 838
Linnéite, 846
Lipowitz's alloy, 792
Liquation, 427, 517, 708, 783
Liquid air, 338
  Claude process, 345
  Fractional evaporation, 343
  Industrial uses, 341
  Linde process, 343
  Pictet process, 344
  Preparation, 339
  Rectifying apparatus, 343
Liquid crystals, 117
  state, 75
Litharge, 708, 785
Lithiophyllite, 607
Lithium, 607
Lithographic plates, 680
Lithopone, 666, 683
Luminescence, 125

Lunar caustic, 712
Luteocobalt salts, 848

Magnalium, 727
Magnesia alba, 673
  Burnt, 670
  mixture, 426
Magnesite, 475, 673
Magnesium, 668
  ammonium arsenate, 426
  compounds, 670–675
  lamp, 670
Magnetic balance, 58
  moment, Specific, 801
Magnetite (magnetic iron ore), 157, 809, 825, 838
Magnus' green salt, 854
Majolica, 742
Malachite, 691, 703
Maletra pyrites burners, 293
Malleability, 511
Mammoth pump, 217, 303
Manganese, 804
  compounds, 805–809
Manganic acid, 804
  compounds, 807
Manganite, 804
Marble, 618–620
  Artificial, 619
Marcassite, 838
Marl, 743
Marsh's arsenic apparatus, 420
Martensite, 828, 830
Martin open hearth (steel) furnace, 823
Martinite, 463
Mass, 1, 8, 9
  action, 67
  Conservation of, 4
  law, 68, 103, 320
Massicot, 785
Matches, 407
Matter, 1, 127
  Unit of, 123
Meat, Frozen, 265
  Preservation of, 258
Mechanical pyrites burners, 294
Meerschaum, 669
Megabasite, 799
Melanterite, 836
Mellitic acid, 438
Melting-point, 111, 792
  diagrams, 517
Mercuric bromide, 690
  chloride, 689
  cyanide, 690
  iodide, 690
  nitrate, 691
  oxide, 689
  sulphate, 691
  sulphide, 691
Mercurous azide, 689
  bromide, 689
  chloride, 688
  nitrate, 689
  oxide, 688
  sulphate, 689
Mercury, 684
  ammonium chloride, 690
  copper iodide, 690
  Extraction, 685
  lamp, 687
  molecule, 50
  Properties, 687
  Statistics, 688
Meta-antimonic acid, 432
Meta-antimonious acid, 431
Meta-arsenic acid, 425
Meta-auric acid, 722
Metaboric acid, 509
Metallisation, 513
Metallography of iron, 828
Metals, 133, 511
  Alkali, 527
  Alkaline earth, 614
  Allotropic forms, 511
  Autogenous welding, 727
  Distillation, 512
  Ductility, 511
  Electrical conductivity, 512
    Temperature coefficient of, 521
  Electrolytic conductivity, 512
  Electromotive force, 521
  General properties, 511
  Heat of combustion, 461
  Heat of fusion, 512, 514
  Magnetic, 513
  Malleability, 511
  Passivity, 512, 794, 811
  Physical constants, 514
  Resistance to sulphuric acid, 284
  Resistivity, 521
  Solid solutions, 514
  Valency, 526
Metaphosphoric acid, 413, 416
Metaphosphorous acid, 413, 415
Metasilicic acid, 502
Metastannic acid, 780
Metatitanic acid, 503
Metavanadic acid, 434
Meyer's molecular weight apparatus, 36
Mica, 724
Microcosmic salt, 613
Micrography, 515, 828
Milch's apparatus for superphosphates, 655
Milk, Cows', 109
  Human, 109
Mill, Ball, 652
  Kent, 652
  Tube, 755, 756
Millon's base, 689
Mineral blue, 843
Miner's lamp, 464
Mining statistics, 450
Minium, 785
Mirabilite, 580
Mispickel, 419
Mohr's (Westphal) balance, 76
  salt, 836
Mol, 26, 65, 99
Molecular heat, 51, 113
  translation, 39
  weights, 34, 85
    Calculation of, 37
    Determination of, 83, 85, 86, 88
Molecules, 32
  Elementary, 33
  Magnitude of, 42, 108
  Monatomic, 50
Mol-ion, 100
Molybdenite, 799
Molybdenum, 373, 799
  nitride, 373
Molybdic anhydride, 799
Monazite, 504, 505
Mond gas, 363
Monotropic substances, 208
Monotropy of sulphur, 208

Montejus, 302
Mordants, 734
Mortar, 618, 747
Mosaic gold, 781
Mottramite, 433
Muffle furnace, 174
Multiple point, 120, 208
Muriatic acid, 169
Murum, 169
Muscovite, 724

Naphthazarin, 282
Nematodes, 495
Neodymium, 502, 775
Neon, 130, 353
Nernst lamp, 506, 671
Nessler's reagent, 235, 690
Neutralisation, Heat of, 63, 101
Newton's alloy, 792
Nickel, 844
    ammonium sulphate, 846
    coinage, 844
    plating, 845
    salts, 846
    tetracarbonyl, 492, 846
Nickeline, 844
Niton, 126, 130
Nitragin, 349
Nitrates, 385
    Solubility diagram of, 541
Nitre, 540
    Cubic, 576
Nitric acid, 383
    Analysis, 401
    Applications, 401
    Concentration of synthetic, 400
    Condensation, 387
    Continuous manufacturing processes, 386
    Degree of concentration, 386
    from ammonia, 398
    Fuming, 383, 401
    Industrial manufacture, 385
    Properties, 383
    Pure, 401
    Specific gravity table, 384
    Statistics, 402
    Synthetic, 390, 398
Nitric anhydride, 377, 382
    oxide, 378
Nitrides, 333, 366
Nitrilesulphuric acid, 331
Nitrogen, 332
    Active, 333
    chloride, 377
    Fixation, 347–51, 390–7
        Biological processes, 348
        Birkeland-Eyde process, 391
        Chemical processes, 350
        Electric processes, 350
    Hydrogen compounds, 376
    iodide, 377
    Linde's process for obtaining, 343
    oxides, 377–82
    Preparation, 333
Nitro-metals, 382
Nitrometer, Lunge's, 578
Nitrosulphonic acid, 290
Nitrosulphuric acid, 381
Nitrosyl chloride, 380
Nitrosylsulphuric acid, 288, 381
Nitrous acid, 381
    anhydride, 377, 380
    oxide, 377
Nordhausen acid, 317
Normal solutions, 99
Novozon, 671

Obsidianite, 310
Occlusion, 134
Ochre, 838
Octaves, Law of, 855
Ohm, International, 520
Oidium, 209
Oil, Animal, 361
    Dippel animal, 404
    of vitriol, 315
Oleum, 315
Olivenite, 706
Opal, 497
Optical properties of gases, 55
Organosols, 109
Orpiment, 419, 421
Orsat gas apparatus, 463
Orthochromatic plates, 714
Orthoclase, 737
Orthophosphoric acid, 413, 415
Orthosilicic acid, 502
Osmium, 851
    compounds, 851
    lamp, 851
Osmometers, 80
Osmon, 445
Osmosis, 80
Osmotic pressure, 80
Ossein, 647
Otto-Hoffmann coke ovens, 452
Oxidation, 189
Oxidisers, 790
Oxone, 553
Oxonium, 91
Oxy-acetylene blowpipe, 191
Oxygen, 16, 187
    Active, 198
    Allotropy, 201
    Analysis, 198
    Chemical properties, 188
    Industrial manufacture, 195, 342
    Laboratory preparation, 193
        Physical methods, 195
    Physical properties, 188
    Sale, 192
    Statistics, 193
    Uses, 190
Oxy-hydrogen blowpipe, 136, 191
Oxyliquit, 341
Oxypersulphuric acid, 274, 329
Ozone, 199
    Analysis, 205
    Applications, 202
    Constitution, 201
    Industrial preparation, 203
    Liquid, 200
    Properties, 200
    Reactions, 200
    Sterilisation of water by, 236
Ozonisers, 203
Ozonium, 188

Palena cement burner, 759
Palladium, 850
    compounds, 851
    hydride, 135, 851
Pandermite, 506
Paramagnetism, 58
Passivity of metals, 794
Pearlite, 830
Peat, 361 *et seq.*, 443
Pentaline, 470

Pentathionic acid, 274, 329
Peptonisation, 108
Perborax, 605
Perbromates, 187
Percarbonates, 475
Percarbonic acid, 475
Perchloric acid, 186
Perhydrite, 270
Perhydrol, 268
Periodates, 187
Periodic system of the elements, 854
Permanent gases, 28
    Liquefaction of, 29
Permanganic acid, 804, 807
    anhydride, 809
Permonite, 609
Permutite, 245
Pernot puddling furnace, 819
Peronospora, 705
Perowskite, 503
Peroxides, 275, 526
Perpetual motion, 7
Persolite, 609
Persulphates, 274
Persulphuric acid, 274, 328
    anhydride, 274
Petalite, 607
Pewter, 428
Phase diagram, 120
    Labile, 581
    rule, 118
Phenomena, Chemical, 3
    Irreversible, 66
    Physical, 2
    Pseudocatalytic, 7
Philosopher's stone, 14
Phlogiston, 16
Phonolite, 529
Phosgene, 492, 772
Phosphamide, 418
Phosphams, 418
Phosphates, 413, 416
    Mineral, 646
Phosphatic manures, 645
Phosphine, 410
Phosphites, 413, 415
    Acid, 415
Phosphonium, 411
    salts, 411
Phosphorescence, 125
Phosphoric acid, 413, 415
    anhydride, 414
    triamide, 418
Phosphorites, 646, 659
Phosphorous acid, 413, 415
    anhydride, 413
Phosphorus, 14, 402
    Allotropic forms, 404
    Amorphous, 406
    Black, 407
    bromides, 412
    Detection of traces of, 403
    Halogen derivatives, 412
    Hittorf's, 404
    hydride, 408
    iodides, 412
    Metallic, 404
    oxides, 413
    oxychloride, 412, 418
    oxyfluoride, 412
    pentachloride, 412
    pentafluoride, 412
    pentasulphide, 418
    pentoxide, 414
Phosphorus, Preparation, 404
    Properties, 403
    Red, 406, 408
    salt, 613
    Statistics, 410
    suboxide, 413
    sulphochloride, 418
    tetroxide, 414
    trichloride, 412
    trifluoride, 412
    trioxide, 413
    trisulphide, 408, 418
    Uses, 407
Photographic developers, 714
    films, 714
    plates, 714
        Autochromatic, 717
        Orthochromatic, 714
        Panchromatic, 714
Photography, 110, 713
    Colour, 716
Phylloxera, 495, 547
Physical phenomena, 2
Pick's salt apparatus, 567
Pigments, Colouring power of, 788
Pinchbeck, 700, 844
Pink salt, 780, 781
Pitchblende, 125
Plants, Assimilatory and Respiratory processes in, 473
Plasmolysis, 83
Platinic acid, 854
Platinised asbestos, 321, 852
Platinodiammonium chloride, 854
Platinotype, 715
Platinous cyanide, 854
Platinum, 852
    black, 852
    chlorides, 854
    Colloidal solution of, 853
    hydroxide, 854
    oxide, 854
    Spongy, 852
    Statistics, 853
Platosemidiammonium chloride, 854
Plücker-Geissler tube, 56
Plumbago, 438
Plumboxan, 198
Pneumatic chemistry, 15
Pollucite, 551
Polonium, 126, 129
Poly-acids and bases, 274, 503
Polymorphism, 115
Polysilicic acids, 502
Polythionic acids, 329
Porcelain, 742
Porphyry, 501
Potash (*see* Potassium carbonate)
    alum, 736
    Caustic (*see* Potassium hydroxide)
    fertilisers, 529
Potassamide, 550
Potassium, 527
    aurate, 722
    aurocyanide, 722
    bicarbonate, 546
    bisulphate, 543
    bisulphite, 544
    bromate, 540
    bromide, 537
    carbonate, 545
        Specific gravities of solutions, 591
    chlorate, 538
    chloride, 534

- Potassium chromate, 797
  - cobalticyanide, 848
  - cyanide, 547
  - dichromate, 797
  - ferrate, 839
  - ferricyanide, 840, 843
  - ferrocyanide, 840
  - fluoride, 537
  - fluosilicate, 537
  - formate, 141
  - hydride, 533
  - hydrogen fluoride, 537
  - hydrogen sulphate, 543
  - hydrosulphide, 271, 544
  - hydroxide, 533
    - Specific gravities of solutions, 555
  - hypochlorite, 537, 572
  - hypophosphite, 410
  - hyposulphite, 544
  - iodate, 540
  - iodide, 537
  - manganate, 807
  - metabisulphite, 544
  - nickelocyanide, 846
  - nitrate, 540
  - nitrite, 542
  - osmate, 851
  - oxide, 533
  - percarbonate, 547
  - perchlorate, 540, 550
  - perferricyanide, 843
  - periodate, 540
  - permanganate, 807
  - peroxide, 533
  - per-ruthenate, 850
  - persulphate, 543, 588
  - phosphates, 550
  - platinocyanide, 854
  - plumbate, 787
  - polysulphides, 544
  - Properties, 528
  - pyrosulphate, 543
  - pyrosulphite, 544
  - ruthenate, 850
  - salts, 529, 532
    - Consumption, 531
    - General reactions, 550
    - Statistics, 530
  - silicate, 547
  - sulphate, 533, 543
  - sulphide, 544
  - sulphite, 544
  - tetrachromate, 798
  - thioantimonate, 433
  - thiocyanate, 841
  - thiophosphate, 418
  - thiosulphate, 544
  - trichromate, 798
  - trithiocarbonate, 495, 547
- Powellite, 799
- Pozzolana, 748, 764
- Praseocobalt salts, 848
- Praseodymium, 502, 775
- Pressure, Absolute, 27
  - constant, 51
  - Critical, 28, 472
  - Osmotic, 80
  - Partial, 73, 619
- Priceite, 506
- Producer gas, 489, 634
- Protyl, 125
- Proustite, 422
- Prussic acid, 497
- Pseudo-solutions, 106
- Psilomelan, 804
- Puddling, 819
  - furnace, 813
- Pulsometer, 302
- Pumice, 739
  - Artificial, 739
- Purple of Cassius, 723
- Purpureocobalt salts, 848
- Pyknometers, 75
- Pyrargyrite, 707
- Pyrites, 291
  - Arsenical, 419
  - burners, 292
  - Burnt, 291, 319, 324, 813, 838
  - Burnt cupriferous, 696
  - Iron, 291, 839
  - Magnetic, 839
  - Manganous, 804
- Pyroantimonic acid, 432
- Pyroarsenic acid, 425
- Pyrolusite, 154, 804
- Pyrometers, Electrical, 850
- Pyrophoric substances, 189
- Pyrophosphates, 417
- Pyrophosphoric acid, 413, 417
- Pyropissite, 446
- Pyrosulphuric acid, 583
  - chloranhydride, 330
- Pyrosulphuryl chloride, 330, 493, 583
- Pyrrhotite, 313, 839

- Quartz, 501, 630
- Quartzite, 740

- Rabdionite, 804
- Radiation of heat, 464
- Radiation, Rutherford's theory of, 127
- Radio-activity, 123
- Radiophone, 221
- Radiothorium, 126
- Radium, 123, 126
  - emanation, 126
- Rare earth elements, 773
- Rare earths for incandescent lighting, 505
- Raspite, 799
- Rays, Anode, 127
  - Canal, 127
  - Cathode, 127
  - Goldstein, 127
  - Ultraviolet, 237
  - X and Röntgen, 127
  - α, β and γ, 127
- Reactions, Bimolecular, 69
  - Endothermic, 61
  - Exothermic, 61
  - Gradual, 73
  - Intermediate, 71
  - Partial, 64
  - Reversible, 66
  - Unimolecular, 69
- Realgar, 419, 421
- Reckleben's reaction, 420
- Red precipitate, 689
- Reduction, 136
- Refractory materials, 739
- Refrax, 500
- Refrigeration, 258
- Regenerative coke furnaces, 454
- Respiration, Intramolecular, 474
- Reverberatory furnace, 173, 693
- Reversible and irreversible processes, 106
- Rheostat, 520
- Rhodamine, 3
- Rhodium, 850

Rhodocrosite, 804, 806
Riché gas, 492
Rock-breaker, 292
Rock crystal, 501
Rongalite, 588
Roscoelite, 433
Roseocobalt salts, 848
Rose's metal, 792
Rotary cement kilns, 760
Rubidium, 551
Rubies, 723, 731
    Artificial, 731
Rust, 810, 838
    Prevention of, 810
Ruthenium, 850
Rutile, 502, 503
Rysager cement furnace, 759

Sal ammoniac, 608
Salt (*see* Sodium chloride)
Salt lakes, 228
Saltpetre (*see* Nitre)
    Chili, 575
        Analysis of, 578
        Statistics, 576, 577
    Prismatic, 576
    Uses, 542
Salts, 274
    Basic, 527
    Complex, 736
    Double, 274, 673
    Double decomposition of, 97
    Mixed, 274
    Neutral, 526
    Nomenclature of, 275
    Solubility diagram of, 535, 541
    Stassfurt, 530, 671
Samarium, 502, 775
Sand, 497
    Normal, 765
    Phosphatic, 647
Sanfillipo sulphur furnaces, 215
Santorino, Terra di, 748
Sapphire, 723, 731
Sassolino, 508
Scagliola, 627
Scandium, 773
Scheelite, 799
Schiff's reagent, 159
Schlippe's salt, 433
Schöffer cement furnace, 759
Schönite, 543, 669, 672
Schütz carbon dioxide process, 476
Schweizer's reagent, 703
Scrubbers, 478
Seger cones, 738
Selenates, 331
Selenic acid, 331
    anhydride, 331
Selenides, 273
Selenious acid, 331
    anhydride, 331
Selenite, 626
Selenites, 331
Selenium, 220, 274
    compounds, 273, 331
Semet-Solvay coke oven, 452
Semipermeable membranes, 80
Senarmontite, 426, 431
Septic tanks, 251
Serpentine, 669
Siderite, 809
Siemens' regenerator (iron) furnace, 816
    gas, 489
Siemens' glass furnace, 453
Sieve, Tetmajer, 765
Sieves, Sizes of, 651
Silica, 497, 501
Silicic acid, 502
    anhydride, 501
Silicides, 498
Silico-bromoform, chloroform, iodoform, 499
Silico-ethane, 498
Silico-methane, 498
Silicon, 497
    compounds, 498–502
Sillimanite, 742
Silundum, 500
Silver, 707
    Amalgamation in America, 709
    Amalgamation in Europe, 708
    compounds, 711–13
    Extraction by lead, 707
    Extraction by other methods, 708–10
    Fineness of alloys, 710
    Horn, 707, 712
    Properties, 710
    Spitting of, 710
    Statistics, 711
Silver-plating, 710
Singer's carbon disulphide apparatus, 494
Slag, Basic, 648, 651, 662, 822
    Blast furnace, 763, 815
Smalt, 419
Smaltine, 846
Smithsonite, 675, 683
Soapstone, 674
Soda (*see* Sodium carbonate)
    Caustic (*see* Sodium hydroxide)
Sodamide, 549, 554
Sodium, 551
    amalgam, 140
    ammonium phosphate, 613
    azide, 607
    bicarbonate, 602
    bisulphate, 387, 582
    bisulphite, 281, 584
    borate, 604
    bromide, 571
    carbonate, 590
        Ammonia process, 596
        Analysis of, 602
        Applications, 600
        Calcining furnaces, 595
        Carbonating, 594
        Crude, 593
        Cryolite process, 599
        Crystals, 595
        Electrolytic process, 600
        Leblanc process, 591
        Solvay process, 596
        Specific gravities of solutions, 591
        Statistics, 600
        Strength, 602
    chlorate, 572
    chloride, 566
        Composition of cooking salt, 569
        Consumption of, 569
        Denatured, 570
        Evaporation of solutions, 568
        Gradation, 568
        Properties, 569
        Statistics, 569
        Uses, 569
    chromate, 797
    cyanide, 547, 607, 675
    dichromate, 797
    ferriaquopentacyanide, 843

- Sodium ferrite, 554
  - ferrocyanide, 841
  - fluoride, 734
  - fluosilicate, 656
  - hydrosulphide, 272, 588
  - hydrosulphite, 586
  - hydroxide, 554
    - Analysis of, 566
    - Chemical preparation, 554
    - Concentration in a vacuum, 562
    - Electrolytic preparation, 555–62
    - Properties of, 554
    - Specific gravities of solutions, 555
    - Statistics, 565
  - hypochlorite, 572
  - hypophosphates, 604
  - hypophosphite, 603
  - Industrial preparation, 552
  - iodate, 572
  - iodide, 571
  - metabisulphite, 584
  - metaperborate, 605
  - metaphosphate, 603
  - metazirconate, 504
  - nitrate, 575
  - nitrite, 579
  - nitroprusside, 843
  - oxide, 553
  - perborate, 605
  - perchlorate, 572
  - periodate, 572
  - peroxide, 553
  - persulphate, 588
  - phosphates, 416, 602
  - phosphite, 603
  - polysulphides, 590
  - Properties, 552
  - pyrophosphates, 603
  - pyrosulphate, 583
  - pyrosulphite, 588
  - Reactions of salts of, 607
  - sesquicarbonate, 602
  - silicate, 606
  - stannite, 779
  - sulphate, 580
  - sulphide, 272, 588
    - Analysis of, 589
  - sulphite, 281, 583
  - tetraborate, 510, 604
  - thioantimonate, 433
  - thioarsenate, 421
  - thiosulphate, 585
  - tungstate, 803
  - uranate, 804
  - zirconate, 504
- Soffioni, 507, 508
- Solar heat, 6, 131, 442
- Solder, 604, 672, 778
- Solfare, 213
- Solfatare, 213
- Solid state, 111
- Sols, 106
- Solubility, 258
  - of gases in liquids, 73, 74
  - product, 706
- Solution, Heat of, 258
  - pressure, 524
    - Electrolytic, 524
- Solutions, Dilute, 80
  - Electrolytic dissociation of, 94
  - Equimolecular, 83
  - Isohydric, 103
  - Isotonic, 83
  - Normal, 99
- Solutions, Saturated, 118, 581
  - Solid, 134, 514
  - Supersaturated, 581
  - Vapour pressure of, 85
- Sombrerite, 402
- Sorbite, 831
- Sorel cement, 672
- Spathic iron ore, 809, 838
- Specific conductivity, 102, 521
  - gravity of liquids, 75
    - solids, 111
    - water, 76
  - heat of gases, 51
    - liquids, 80
    - metals, 512, 514
    - solids, 111
  - resistance, 521
  - volume, 42, 73, 75
- Spectroscope, 57
- Spectroscopy, 55
- Specular iron ore, 809
- Spectrum, Absorption, 57
  - Continuous, 55
  - Emission, 56
- Sphene, 503
- Spinel, 733, 795
- Spitting of metals, 512, 710
- Stannic compounds, 780–1
- Stannous compounds, 779–80
- Steatite, 668, 674
- Steel (*see* also Iron), 810, 820
  - Bessemer process for, 821
  - Cast, 811, 821, 824
  - Cementation, 811, 824
  - Chrome tungsten, 827
  - Crucible, 824
  - Electric processes for, 824
  - Eutectic, 830
  - Form of sparks from, 827
  - Hardening of, 820
  - Héroult process for, 824
  - Hypereutectic, 830, 832
  - Hypoeutectic, 830, 832
  - Kjellin process for, 824
  - Manganese, 827
  - Manganese vanadium, 826
  - Martin process for, 823
  - Micrography of, 828
  - Nickel vanadium, 826
  - Normal, 831
  - Properties of, 826
  - Puddled, 811
  - Rapid, 826
  - Rapid chrome, 827
  - Refining of, 822
  - Self-tempered, 827
  - Silicon, 826, 833
  - Stassano process for, 824
  - Statistics of, 831, 834
  - Tempering of, 820
  - Titanium, 826
  - Tungsten, 832
- Stenolytes, 97
- Stereochromy, 606
- Stereoisomerism, 125
- Sterilisation of water, 236
- Stibnite, 426, 432
- Stoichiometric value, 21, 48
- Stolzite, 799
- Stone, Artificial, 745
  - Lithographic, 619
  - Soap, 674
- Stoneware, 741
- Strass, 629

Stromeyerite, 707
Strontianite, 662, 663
Strontium, 662
Stucco, 628
Stupp, 686
Sürth carbon dioxide plant, 478
Sulphamide, 330
Sulphaminic acid, 330
Sulpharsenic acid, 422
Sulpharsenious acid, 422
Sulphatotetramminoplatinum hydroxide, 849
Sulphimide, 330
Sulphonic acid, 331
Sulphonitrous acid, 290
Sulphur, 205
    Allotropic forms, 206
    Analysis, 219
    bromide, 273
    burners, 296
    calcaroni, 214
    Chemical properties, 209
    Colloidal, 207
    Commercial varieties, 210
    dichloride, 273
    dioxide (*see* Sulphurous anhydride)
    Enantiotropy of, 208
    Extraction of, 213
    Flowers of, 218
    furnaces, 215
    Ground, 219
    Halogen compounds of, 273
    heptoxide, 274
    hexafluoride, 273
    Liver of, 544
    Magister of, 207
    monochloride, 273
    Native, 213
    ores, 214
    Physical properties, 206
    Precipitated, 207
    Recovery processes, 596
    Refining of, 218
    sesquioxide, 274, 282
    Statistics, 210
    tetrachloride, 273
    trioxide (*see* Sulphuric anhydride)
    Uses of, 209
    Winnowed, 219
Sulphuric acid, 274, 282
    Amino-derivatives, 330
    Analytical control of manufacture, 312
    anhydride, 314
    Applications, 284
    Chloro-anhydrides of, 329
    Concentration, 307
    derivatives, 328
    for accumulators, 311
    Freezing-point diagram, 317
    from gypsum, 307
    Fuming, 314, 315, 317
    Lead chambers, 296
        Control of, 306
        Falding, 314
        Tangential, 298
    Manufacture, 287, 290
    Manufacturing yields, 312
    Properties, 282
    Purification, 311
    Resistance of metals to, 284
    Specific gravity table, 286
    Statistics of production, 285, 313
    Theory of formation in lead chambers, 288, 313
    Vapour pressure table, 283
Sulphuric anhydride (Sulphur trioxide), 274, 314
    Catalytic process for, 319
    Preparation of, 318
    Properties, 315
Sulphurimeter, Chancel's, 219
Sulphurous acid, 274, 281
    anhydride, 275
    chloro-anhydride, 330
Sulphurous anhydride (Sulphur dioxide), 274, 275
    Application and statistics, 278
    Liquid, 277, 280
Sulphuryl chloride, 330
Sun, Composition of the, 59
Superphosphate, 645
    Analysis, 650
    Double, 659
    Dryer for, 657
    Industrial processes, 651
    Mechanical dischargers, 655
    Milch's apparatus, 655
    Mixers, 653
    Sampling, 650
    Statistics, 648, 659
    Strength, 650
    Theory of manufacture, 648
    without sulphuric acid, 657
Surface combustion, 464
    tension of liquids, 84
Suspensoids, 106
Sylvine, 149, 530, 531, 534
Sylvinite, 533
Symbiosis, 349
Symbols, Alchemical, 43
    Chemical, 44
Synthesis, 45

Tachydrite, 620
Tachyol, 712
Talc, 668, 674, 740
Tanning, 110
Tantalites, 434
Tantalum, 434
    lamp, 435
Tantiron, 310, 400, 819
Tar, Vacuum, 442
Tartar emetic, 428, 431
Telephony, Wireless, 221
Telluric acid, 331
    anhydride, 331
Tellurium, 221, 273
    Oxygenated compounds of, 331
Tellurous acid, 331
Temperature, Critical, 28
    of flame, 465
    of reaction, 70
    of voltaic arc, 465
Temperatures, Absolute, 25
    Critical, 28
    Cryohydric, 514
    Freezing, 621
    Measurement of, very high, 738, 850
    of atmosphere, 336
    of ignition, 189
Terbium, 502, 773
Terra-cotta, 742
Tetmajer sieve, 765
Tetraboric acid, 509
Tetramminocobaltipotassium nitrite, 848
Tetraphosphate, Italian, 658
Tetrathionic acid, 274, 329
Thallium, 772, 773
Thénardite, 580

Thermit, 727
Thermochemistry, 60
Thermodynamics, 51
Thermometer, Beckmann, 87
    for low temperatures, 30
Thioantimonic acid, 433
Thioarsenates, 422
Thiocyanates, 548
Thionyl chloride, 330
Thiophosphites, 408
Thiosulphuric acid, 274, 329
Thorium, 126, 502, 504
Thulium, 773
Thyroiodin, 162
Tiles, 743
Tin (*see* also Stannic and Stannous), 776
    amalgam, 778
    Butter of, 780
    dioxide, 780
    foil, 777
    Grey, 777
    hydroxides, 779, 780
    oxychloride, 779
    oxysulphide, 781
    perchloride, 780
    plate, 778
    Production, 778
    Properties, 777
    salt, 779
    scrap, 777
Tinkal, 506, 508
Titanates, 503
Titanic acid, 503
Titanite, 503
Titanium, 502
Tiza, 507
Tofani (carbide) furnace, 640
Touchstone, 721
Tourilles, 173
Tradescantia discolor, 83
Transmutation of the elements, 130
Transport numbers, 103
Trass, 748
Triamminocobalt salts, 848
Triazoiodide, 377
Tricalcite, 706
Tridymite, 630
Trielino, 470
Triethyl silicoformate, 498
Triphyllite, 607
Triple point, 120, 122, 208
Trisulphaminic acid, 331
Trithiocarbonic acid, 496
Trithionic acid, 274, 329
Tro-na, 602
Troostite, 830
Troosto-sorbite, 831
Troposphere, 336
Tube mills, 756
Tungsten, 799
    Colloidal, 802
    compounds, 802
    lamp, 801
Tungstic acid, 802
    anhydride, 802
Tyndall's phenomenon, 107
Type metal, 428
Typhoid, 231
Tyrolite, 706

Ulexite, 507
Ultramarine, 770
Ultramicroscopy, 107
Ultra-violet rays, 237
Ultra-violet lamp, 238
Unit of energy, 61
    force, 27, 61
    heat, 61
    resistance, 520
    work, 61
Units, Absolute, 27
    Electrical, 519
Unity of matter, 123, 128, 858
Univariant systems, 121, 208
Uraninite, 125, 803
Uranite, 803
Uranium, 129, 803
    nitride, 373, 803
    salts, 803
Uranyl compounds, 803
Urao, 590
Urea, Fermentation of, 356

Vacuum concentration apparatus, 562
    tar, 442
Valencies, Principal, Secondary, etc., 48
Valency, 46
    Constant, 47
    of ions, 98
    of metals, 526
    Variable, 47, 99
Valentinite, 426, 431
van der Waals equation, 41
Vanadates, 434
Vanadic acid, 434
Vanadinite, 433
Vanadium, 433
    salts, 434
Vapour pressure, 85
    of water, 224
Vapours, Density of, 34
Varec, 158
Varvicite, 804
Vaterite, 618
Velocity of molecules, 39
    reaction, 64, 67, 70
Verdigris, 699
Vermilion, 691
Vicat's needle, 765
Vine mildew, 705
Vitriol, Blue, 703
    Green, 836
    Oil of, 282
Vivianite, 402, 837
Volt, 519
Voltaic series of the elements, 521
Voltameter, Garuti, 144
Volume, Atomic, 56, 856
    Critical, 28
    Molecular, 26
    Specific, 42, 75
Volumenometer, 111
Volumetric analysis, 99
Vulpinite, 626

Wackenröder's liquid, 329
Water, 222
    Analysis, 234
    Artificial mineral, 255
    Boiler feed, 241
    Chemical properties, 227
    Composition of, 223, 232
    Dielectric constant of, 95
    Dissociation of, 101
    Distilled, 253
    Drinking, 230
    Effluent, 110, 532, 671
        Purification of, 249

Water, Ferruginous, 247
  Filtration, 235
  for industrial purposes, 239
  gas, 137, 138, 143, 365, 486
    Calorific value, 487
  glass, 606
  Hardness of, 239
  Heat of evaporation, 226, 242
  Lake, 228, 232
  Manganiferous, 248
  Meteoric, 223
  Natural mineral, 254
    Radioactivity of, 255
  of crystallisation, 227
  of Dead Sea, 228
  Physical properties, 223
  Potable, 230
  power, 518
  Provision of drinking, 229
  Purification for drinking, 235
  River, 228, 232
  Sea, 228, 530
    Distillation of, 252
  Separation of iron from, 247
  Softening of, 241
  Specific gravity at different temperatures, 76
  Sterilisation, 236
  Subsoil, 232
  Surface, 228
  Synthesis, 31
  tanks, 230
  Treatment for industrial uses, 241
  Vapour pressure, 224
Waterproof fabrics, 734
Watt, 62, 519
Wavellite, 402
Weber's acid, 288
Welding, Autogenous, 727
  of aluminium, 727
Wells, Artesian, 230
  Norton or American, 230
Westphal balance, 76
White, Fixed, 666
  metal, 428
  precipitate, 690
  Zinc, 682, 788
White lead, 788
  Manufacturing processes, 789
  Russian, 790
Witherite, 663, 667
Wolframite, 799
Wollastonite, 628
Wolter's reaction, 185
Wood's metal, 792
Wool, Carbonisation of, 734
  Philosopher's, 680
Wotan lamp, 801
Wulfenite, 782

Xanthocobalt salts, 848
Xenon, 353
Xylolite, 672

Yellow, Chrome, 798
  Naples, 428
Ytterbium, 775
Yttrialite, 775
Yttrium, 775

Zeolites, 245
Zero, Absolute, 25
Zimalium, 727
Zinc, 675
  Butter of, 682
  Crude, 679
  dust, 677, 680
  Electrolytic manufacture of, 679
  green, 682
  Properties of, 679
  Refining of, 679
  salts, 681–4
  Spathic ore, 683
  white, 682
Zirconium, 503

PRINTED IN GREAT BRITAIN BY RICHARD CLAY & SONS, LIMITED
BRUNSWICK ST., STAMFORD ST., S.E. 1, AND BUNGAY, SUFFOLK.