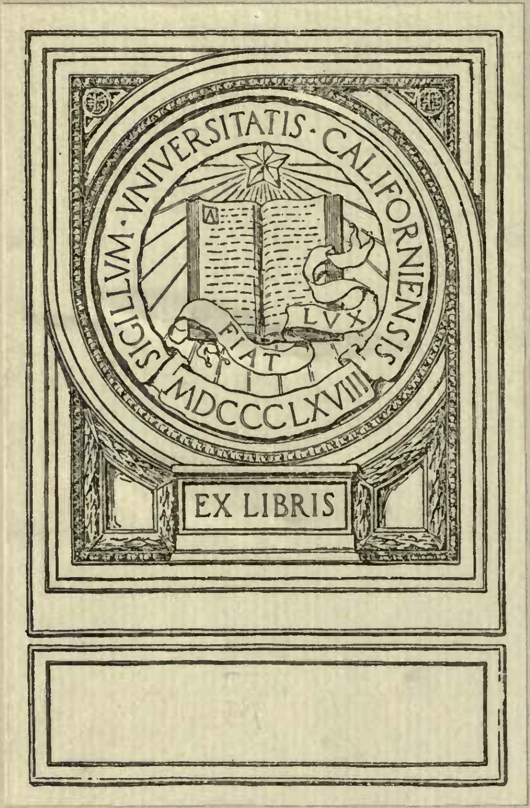

TREATISE ON
GENERAL AND INDUSTRIAL
ORGANIC CHEMISTRY

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ORGANIC CHEMISTRY

BY

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TRANSLATED FROM THE THIRD ENLARGED AND REVISED ITALIAN EDITION BY

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PART I

WITH 254 ILLUSTRATIONS

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TRANSLATOR'S PREFACE

In this translation it has been deemed undesirable in most cases to convert the metric weights and measures into those of the English system, but, in general, prices are given in British currency, twenty-five lire being taken as the equivalent of one pound sterling. Where quantities are given in tons, the latter are to be read as metric tons of 1000 kilograms or 2204·6 lb. avoirdupois.

The abbreviations employed for the different units of weights and measures are those in common use, and temperatures are expressed in degrees Centigrade in all cases.

THOMAS H. POPE.

PREFACE TO THE THIRD ITALIAN EDITION

The second edition of this treatise, which appeared in 1913, has been exhausted for over two years, while the Spanish and English versions have also been completely sold. The publication of this new edition has been delayed owing to the vicissitudes of the war, which, although apparently at an end, has left industrial, commercial and social upheaval behind it. The most serious and urgent problem now preoccupying all so-called civilised countries is that of *production*, which should lead to the rapid recovery of the wealth and reserves destroyed by the monstrous conflict which sacrificed, on the altar of international imperialism, upwards of fifteen millions of human lives.

A clamant need is the speedy transformation of the improvised and superfluous industries of war into peace industries. Never before have the interests of humanity imposed such serious tasks on the technologist, particularly on the chemist.

The aid of science is necessary in order to arrive, as rapidly and economically as possible, at the most intense production of the materials furnished by nature and consumed by society. This is necessary in the interests of all, since, even when the legitimate restlessness of nations sacrificed by the dominating castes shall have resulted in a new social order, less barbarous, less chaotic and less unjust than that now in force, increased output will be more than ever of importance for the welfare of the new humanity.

In this edition, from which new English, French and Spanish editions are being prepared, account is taken of the industrial progress in the various branches of chemistry and of statistical data up to the end of the year 1913.

For the period of the war, only data referring to Italy can be guaranteed. The statistics and prices for the years of war are of transitory importance and are recorded as curiosities reflecting the abnormalities of this historic period. Fiscal tariffs cannot be given, since in all countries these have undergone change and will not be systematised for some time yet.

THE AUTHOR.

MILAN.

PREFACE TO THE FIRST ITALIAN EDITION

A NEW treatise on Organic Chemistry might, in view of the existence of the excellent works of Bernthsen and Holleman, be considered superfluous.

Both of these books, which differ little in the manner in which the subject is developed, are, however, confined to a theoretical and systematic exposition of the many organic compounds, the industrial side of the question and the applications of these compounds being almost entirely neglected. It is hence difficult for the student to ascertain which of the thousands of substances described are really of practical importance.

Modern teaching of chemistry adheres in a too one-sided manner to the old but fruitful idea of Liebig, that "to obtain a sound practical man it is necessary to train a good theorist." This conception was taken too literally, although it gave good results when chemical industry was in its infancy, since in those days any theorist could easily introduce new and important methods. But to-day, when the industry has attained the adult stage—has advanced to such an extent and become so varied and complex, being stimulated incessantly by keen national and international competition, which demands rapid changes and improvements—the valuable time of the young technician cannot be wasted in a protracted and sometimes sterile apprenticeship. Present-day conditions require, therefore, some such expansion of Liebig's maxim as the following: In order to produce, rapidly and with increased certainty, a sound, practical man, it is necessary to train a good theorist and to initiate him into both the theoretical and the practical study of the more salient industrial problems.

It does not suffice that the young chemist, about to begin his industrial or teaching career, should have a thorough knowledge, for instance, of the various syntheses and constitutional formulæ of the sugars. He should also be acquainted with at least the general outlines of the industrial processes and of the technique of the manufacture of sugar, beginning with the slicing of the beets and proceeding to the exhaustion of the pulp, defecation, saturation, filtration with filter-presses, boiling, and vacuum concentration in multiple-effect apparatus, refining and centrifugation of sugar crystals, utilisation of residues, and so on. He should, indeed, understand the plant and chemical processes of the more important industries, as these often find application in the manufacture of products of a secondary or entirely new character.

What would avail a study of the wonderful artificial colouring-matters derived from coal-tar, with the inexhaustible syntheses composing their theoretical basis, if it were limited to a simple mnemonic exercise for the student and no notice were taken of the interesting practical applications to the dyeing of the various textile fibres?

Nor should the young student ignore statistics of production; he should be able to appreciate the importance of variations in the exportation and importation of the principal chemical products, and to judge of the economic and social conditions with which such variations correspond.

After a brief novitiate, he should be in a position to point out the more striking technical defects and the more marked difficulties met with in particular industrial processes and to suggest rational and not fanciful remedies.

It is this space, the vacant region representing a suitable fusion of theoretical with applied chemistry, which requires filling. This I have attempted in the present work, which of itself is certainly insufficient to cover the whole of the ground.

The difficulties encountered in preparing the volume on Inorganic Chemistry are multiplied in dealing with Organic Chemistry, and this is the case as regards the collection and confirmation, not only of the statistical data but of the chemical processes giving the best results in practice. For in any particular industry it has often been found that the results of investigations are in such disaccord with the practical data as to render it a matter of great uncertainty what conclusions should be presented to the reader.

Inquiries addressed to manufacturers resulted in aggravation of this uncertainty, what was confirmed on the one hand being denied on the other, and plant guaranteed by one firm to be the best being decried by a competing firm. It hence became necessary to apply directly to the operatives working a given process and to draw conclusions from the whole of the data and information thus obtained.

It is thus that readers may explain the contradictions between different authorities on one and the same subject, and also the fact that the conclusions reached by the author with reference to certain industrial processes are not always in accord with those given in other treatises.

The intention has certainly not been to prepare a complete treatise on technological chemistry and still less on chemical technology. The work having to be restricted within limits of space approximating to those of vol. i, the author has descended to details only with some of the principal industries and especially with those best adapted to give a general idea of the different applications of chemical processes and of chemical technics.

To this end the author has dwelt preferably on the industries of illuminating gas, sugar, alcohol, beer, acetic acid, dyeing, textile fibres, fats and soaps, explosives, etc.

From these examples the student may gather much instruction applicable to many other industries not dealt with in detail.

Repetition has been avoided and time and space saved by frequent references to arguments already developed in vol. i, *Inorganic Chemistry*.

Advice and collaboration are desired from readers and colleagues in order that gaps in the present work may be filled and inaccuracies and defects remedied.

E. MOLINARI.

MILAN.

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PART I. GENERAL

In Vol. I. of this treatise[1] is given a brief summary of the history of chemistry and of those portions of physico-chemical theory which are necessary for the interpretation of chemical phenomena.

Hence, this course of organic chemistry assumes in the reader a knowledge of the fundamental chemical laws and ideas, methods of determining molecular weights, and so on.

The separate treatment of the carbon compounds, which is termed *organic chemistry*, is a purely didactic convenience and somewhat of a habit, there being no sound foundation to justify a distinction between organic and inorganic chemistry.

This division of the subject dates back to the time of Lemery, who, in 1675, regarded the substances of the animal and vegetable kingdoms as distinct from those of the mineral kingdom, and to 1820, when Berzelius justified the separation by stating that the preparation of organic compounds required the intervention of *vital force*, whilst inorganic compounds could be prepared artificially in the laboratory. This view was, however, abandoned when, in 1828, Wöhler succeeded in preparing *urea* (found in urine) from inorganic material in the laboratory, and when, later, acetic acid was prepared artificially. Subsequently, the number of so-called organic compounds obtained synthetically has increased almost without limit.

There exists to-day no reason for a distinction between organic and inorganic compounds; the first comprise a group of carbon compounds embracing an immense number (over 150,000) of substances, which exhibit certain common characters and are conveniently studied by themselves.

It had already been recognised by Lavoisier that all so-called *organic* compounds, originating in *organised* bodies, contain *carbon*, *hydrogen*, and *oxygen*, and that many of them, especially those of the animal kingdom, contain also *nitrogen* and sometimes *sulphur*, *phosphorus*, *halogens*, and *metals*.

The study of organic compounds is as old as the human race, which, from the most remote times, has prepared alcohol and acetic acid from vegetable juices (the must of the grape and other fruit, etc.).

After the discoveries of Lavoisier and the investigations of Berzelius, organic chemistry began to acquire special importance, and Liebig, by introducing simple and exact methods for the analysis of organic compounds, rendered most valuable help to the wonderful theoretical and practical development which has been shown by this branch of chemistry during the past fifty years, and which has been largely responsible for the impulse given to progress and civilisation in the nineteenth century.

In order to study the innumerable derivatives of carbon, to be able to obtain separate individuals and to characterise them by means of their chemical and physical properties, then to group and classify them and to deduce in a more or less general way the laws they obey, it was necessary to isolate and prepare in the *pure* state these separate chemical individuals.

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[1] E. Molinari, "Inorganic Chemistry"; translated by T. H. Pope, 1920.

PURIFICATION OF ORGANIC SUBSTANCES

The purification of organic substances is not so easy to effect as might at first appear. Pure substances are characterised by certain physical constants (boiling-point, melting-point, crystalline form, etc.), which serve to show if a substance is in a suitable condition for chemical analysis.

The chemical processes of *purification* may be deduced from the chemical properties of the substances themselves, as described in Parts II and III of this treatise; general physical methods effect *purification by means of suitable solvents* (water, alcohol, ether, light petroleum, acetic acid, benzene, acetone, chloroform, carbon disulphide, etc.), which separate certain substances from others more or less soluble; or, in many cases, purification is brought about by *crystallisation,* a solution of the impure substance in a suitable hot solvent depositing—on gradual cooling or partial evaporation of the solvent—the pure substance in characteristic and well-defined crystalline forms, which may be controlled by measuring the angles and determining the axial ratios of the crystals.

Impurities separate sometimes before and sometimes after the crystallisation of the substance under examination, so that recourse is had to *fractional crystallisation,* which, when repeated, may give excellent results.

In certain cases, substances are purified by *sublimation.*[1] When pure, a liquid has a constant *boiling-point* for a definite pressure (Vol. I., p. 85), and this is determined by *distilling* the liquid in a flask with a lateral tube, a thermometer being arranged in the neck of the flask without its bulb dipping into the boiling liquid. The temperature of the vapour gives the boiling-point of the liquid; the vapour escapes from the side-tube and is condensed by means of a *Liebig's condenser,* formed of an inclined glass tube surrounded by a wider tube through which water circulates from the lower to the upper end (Fig. 2).

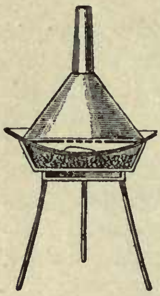
Fig. 1.

The boiling-point of a very small quantity of substance may be accurately determined by means of the arrangement shown in Fig. 3: a few drops of the liquid are introduced into a small tube, *d*, closed at the bottom and drawn out into a narrowed part. Into the liquid dips a capillary tube, sealed at the point *a* by fusing the glass. The tube is attached to the thermometer, *c*, and the whole immersed, to the depth of a few centimetres, in a liquid having a boiling-point higher than that of the liquid under examination. Heat is now gradually applied, superheating being prevented by the air-bubbles issuing from the lower end of the capillary tube. When the boiling-point is reached, bubbles form very rapidly at the bottom of the liquid, and the boiling-point is read off on the thermometer.

Certain substances which readily decompose on boiling at the ordinary pressure can be distilled unchanged at a constant, but somewhat lower, temperature by lowering the pressure, *i. e.*, by distilling in a vacuum (*see later*). For this purpose use is made of a mercury or water pump (Sprengel).

When two liquids are mixed, they may be separated almost completely by *fractional distillation,* if there is a wide interval of temperature between their boiling-points. In consequence of the partial pressure of the components, at different temperatures mixtures distil over which contain varying proportions of these components; the liquid with the lower boiling-point first preponderates in the distillate, while at higher temperatures that with the higher boiling-point predominates. On repeated redistillation of the two extreme fractions separately, the two liquids may be obtained in the pure state. In certain cases, however, a mixture of two liquids does not exhibit a regular progression in the vapour pressure corresponding with the preponderance of one or other of the two components. There are, indeed, liquids which, when mixed in certain proportions, show a minimum vapour pressure—lower even than that of the less volatile component—whilst,

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[1] *Sublimation* takes place with many solid substances and consists in the passage from solid to vapour on gentle heating, and from the state of vapour to the solid crystalline condition when the vapours come into contact with a cold body, these changes taking place directly and not by way of the liquid state. Usually the substance is placed on a clock-glass, covered by a perforated filter-paper and by a funnel; when the clock-glass is heated on a sand-bath, the pure sublimed crystals collect on the walls of the funnel (Fig. 1). In some cases, the sublimation is carried out in a vacuum.

on the other hand, a mixture of two liquids sometimes has a vapour pressure greater than that of its more volatile constituent; the two liquids cannot then be separated by fractional distillation, especially when their boiling-points are not far apart.[1] In these cases good results are obtained practically by employing so-called *rectification*, this consisting in distilling the liquid mixture through a Le Bel and Henninger (1874) rectifying tube (Fig. 4), which is fitted at regular intervals with discs of platinum gauze, and above these takes the form of a series of two or more bulbs, a lateral tube being so placed as to lead the liquid condensing in any bulb back to the bulb below it. When the liquid boils, the mixed vapours pass up the tube and meet the first gauze disc, where the vapour of the less volatile liquid is condensed in greater proportion than the other, so that the vapour reaching the second gauze is richer in that of the more volatile liquid; a similar process occurs at the successive gauzes and in the bulbs above them, so that the vapour passing through the uppermost bulb is that of the more volatile liquid, and this passes down the side-tube (at the mouth of which the thermometer is placed) to the condenser. During this rectification the cooling produced by the outer air and the consequent condensation of the vapours result, in the rectifying tube, in a stream of liquid flowing down the walls of the tube; this liquid film meets the ascending vapours and gives up to them its more volatile constituent and takes up from them their less volatile component, so that only the vapour of the more volatile liquid reaches the top of the tube, while the less volatile liquid is returned.

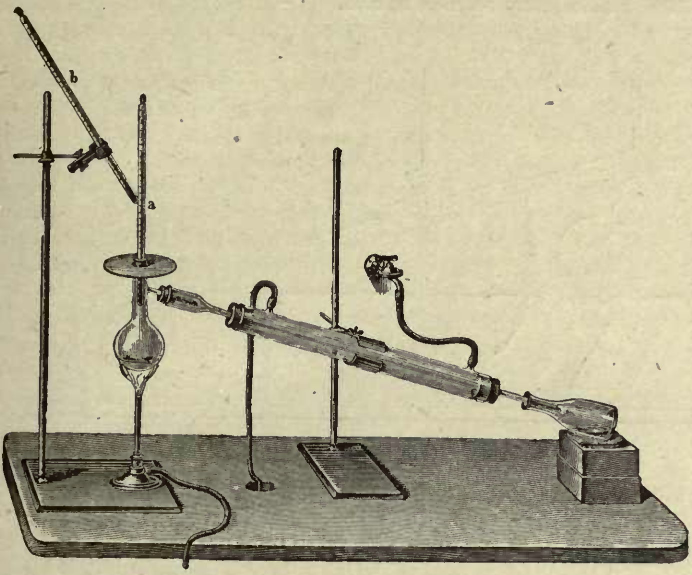

FIG. 2.

FIG. 3.

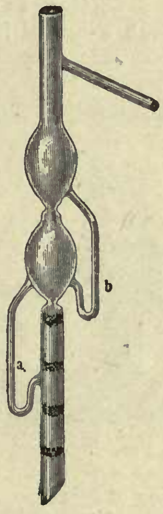

FIG. 4.

FIG. 5.

Similar results are obtained by *Hempel's rectifying column* (1881), which is filled with glass beads (Fig. 5). With this also the phenomenon of rectification which goes on often

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[1] *Theory of Fractional Distillation.* We shall see later the relations existing between the boiling-point and the composition and chemical constitution of organic substances (homologous series, isomerides, etc.). Of interest at the present juncture is the behaviour on distillation of a mixture of two liquids which dissolve one in the other in all proportions.

According to Wanklyn and Berthelot, when a mixture of equal weights of two liquids is distilled, the proportions of the two in the distillate depend not only on their proportions in permits of the separation of liquids with boiling-points quite close together. This phenomenon has important applications in the alcohol industry (*see later*), in the manufacture of oxygen and nitrogen from *liquid air*, in the preparation of liquid sulphur dioxide (Vol. I., pp. 280 and 340), and in many other industries.

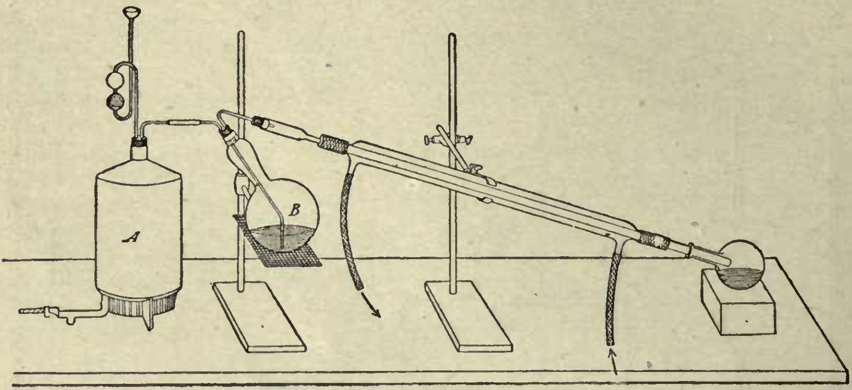

Fig. 6.

In many cases substances (liquid or solid) are purified by distillation in a current of steam, certain of them being volatile under these conditions even when their boiling-points are above that of water; in the distillate the substance often separates owing to its insolubility in water. An arrangement used in the laboratory is shown in Fig. 6, steam being generated in *A* and passing through the substance to be distilled in the flask, *B*, which may be heated directly with a flame.

In some instances the distillation is effected by means of *superheated steam* (150° to 350°), which is obtained by passing steam through a coil of iron or copper tubing heated with a bunsen burner (Fig. 7).

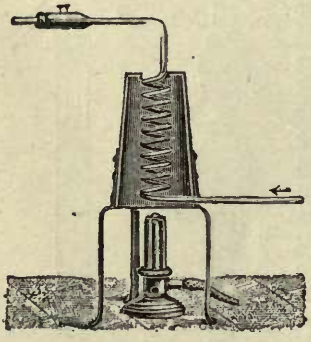

Fig. 7.

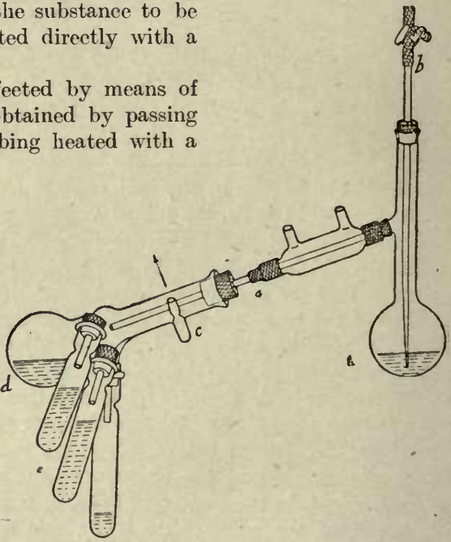

Fig. 8.

A number of substances decompose when heated at the ordinary pressure, whilst they distil unchanged in a more or less perfect vacuum, owing to a marked lowering of the

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the original liquid and on their vapour pressures at the boiling-point of the mixture itself, but also on the reciprocal adhesion of the constituent liquids and on their *vapour densities*. When a mixture of two miscible liquids, in equal weights, is distilled, the quantity of each component which distils may (disregarding certain exceptions) be calculated by multiplying the vapour pressure (at the boiling-point of the mixture) by the vapour density. Hence it can be understood how, in some cases, the less volatile substance distils in greater quantity. Even if the vapours that distil over contain equal volumes of the two vapours (that is, equal numbers of molecules), the condensed liquid will contain a greater proportion by weight of the constituent with the higher molecular weight. This explains why water, with a low vapour density, causes boiling-point. Of the many different forms of apparatus employed in the laboratory for this purpose, that of Bredt is illustrated in Fig. 8. An ordinary thick-walled distilling flask, *A*, is used, its side-tube being connected with the condenser *a* and with the collecting apparatus, which consists of a flask, *d*, and three tubes, *e*, of thick glass, and is joined to the condenser by means of a perforated stopper; the pump by which the air is withdrawn from the whole apparatus is connected with the tube *c*, which communicates also with a manometer to show the extent of the vacuum attained. Superheating and consequent bumping of the liquid are avoided by the insertion of the tube *b*, the lower end of which is drawn out to a capillary and dips below the surface of the liquid, while the upper end is closed with a piece of rubber tubing fitted with a screw-clip; by means of this tube, into which also the thermometer may be introduced, a slow current of air or other inert gas, controlled by means of the screw-clip, is allowed to bubble through the liquid during the distillation. The flask is heated in a bath of oil or fusible alloy, and, if the distillate is very dense, no water need be passed through the condenser. The first portion distilling over at a definite temperature is collected in *d*, and when the temperature rises suddenly, the collecting apparatus is rotated so that the distillate is collected in one of the tubes, *e*; when the thermometer no longer indicates a constant temperature another of the tubes, *e*, is employed, and so on.

MELTING-POINT. Whilst with liquids the boiling-point is generally used as a criterion of purity, for solids the melting-point is mostly employed for this purpose, and in certain cases also the boiling-point. So long as the substance is impure, the melting-point is usually too low. The melting-point is determined by introducing a few centigrams of the substance into a very narrow, almost capillary glass tube, closed at the bottom

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substances with higher boiling-points (ethereal oils, naphthalene, etc.) to distil, since, although the latter have low vapour pressures, their molecular weights are high.

Of frequent occurrence are mixtures of two miscible (one in maximum or minimum ratio to the other) liquids, which, on distillation, do not separate, but distil together in unaltered proportions at constant temperature. Thus, 16 parts of alcohol and 84 of CCl_4 boil at 64·9°, and 32 parts of alcohol and 68 of benzene at 67·8°; if 59·8 parts of CCl_4 (b.-pt. 76·4°) are added to a mixture of 12 parts of alcohol with 32·2 of benzene, which begins to boil at 67·8°, the boiling-point of the ternary mixture falls to 65·8°. Further, alcohol, water, and benzene in certain proportions yield a ternary mixture which boils at a lower temperature than any of its separate components and cannot be separated into the latter; if, however, excess of benzene is added, repeated distillation yields the benzene and water together with part of the alcohol, so that pure alcohol finally remains (Young, 1894 and 1902; Kablukov, Solomonov, and Galine, 1903; Golodetz, 1912). A mixture of 31 per cent. of acetic acid (b.-pt. 118°) with 69 per cent. of toluene (b.-pt. 110·4°) boils completely without separation at 104°. With 2 per cent. of acetic acid, benzene (b.-pt. 80·4°) forms an inseparable mixture boiling at 80°, which is the minimal boiling-point for benzene-acetic acid mixtures. If to 100 grams of the above toluene-acetic acid mixture are added 1800 grams of benzene (rather more than is required to give a benzene-acetic acid mixture with 2 per cent. of the acid), the liquid commences to boil at 79·6°, and up to 81·8° 1900 grams distil, containing always about 1·85 % of acetic acid, the residue consisting of 31 grams of *pure* toluene. Toluene containing 19·6 per cent. of water boils unchanged at 84·1°, and if 67 grams of water are added to 400 grams of the above toluene-acetic acid mixture, distillation yields in succession, (1) between 84° and 85°, 355 grams containing all the toluene and about 4 per cent. of acetic acid, which is separable by a further distillation, (2) about 28 grams of 65 per cent. acetic acid, and (3) about 82 grams of 95 to 98 per cent. acetic acid, about one-half of this being of 100 per cent. strength. A mixture of 60·5 grams of benzene, 242 grams of toluene, and 39·5 grams of methyl alcohol (the last gives with 60·5 per cent. of benzene a mixture boiling unchanged at 58·35°) yields at 58·2° to 59·8°, 94 grams containing methyl alcohol and benzene in the above ratio, and at 110°, 228 grams of pure toluene. From a mixture of benzene and methyl alcohol, pure benzene may be separated by distillation in presence of carbon disulphide.

On distilling a mixture of two liquids not soluble one in the other, the corresponding vapours do not influence one another, and the total pressure of the vapours is given by the sum of the pressures of the two liquids at the temperature of distillation. The boiling-point of the mixture is the temperature at which the sum of the vapour pressures of the components equals the atmospheric pressure; it should be mentioned that the boiling-point of such a mixture is necessarily lower than that of the more volatile liquid, since here also *Dalton's law of partial pressures* (Vol. I., pp. 73, 619) holds. Naumann (1877) showed that, in the vapour distilling from such a mixture, the ratio between the volumes of the components corresponds with the ratio between the vapour pressures of the two liquids at the boiling-point of the mixture; hence the *weights* of the two components are obtained by multiplying these ratios by the corresponding densities (or molecular weights). By means of this rule, Naumann succeeded in determining the molecular weights of various substances simply by distilling mixtures of them. A mixture of water and isoamyl alcohol (b.-pt. 135°) has a constant boiling-point of 96°, and distils continuously in the ratio of two volumes of water and three volumes of the alcohol.

(Fig. 9), the tube being attached to the bulb of a thermometer dipping into a beaker of concentrated sulphuric acid, oil, or paraffin wax, which serves to transmit heat to the substance. A small glass stirrer serves to prevent superheating of the liquid, and, when the substance is pure, it melts entirely within a degree and generally becomes transparent. When the temperature of the bath approaches the melting-point, the flame is lowered and the bath heated gently so that the temperature rises half a degree every four or five seconds; only in exceptional cases should rapid heating be continued.[1]

To determine the melting-point of a fat, a tube drawn out to a capillary and sealed at the lower end (Fig. 10*a*) is held in an inclined position, and one or two drops of the fused and filtered fat introduced into the enlarged part (Fig. 10*a*, *A*). When the fat is solidified, the tube is kept in a cool place for twenty-four hours, after which it is attached vertically to the bulb of a thermometer; it is then heated in a suitable bath, note being taken of the temperature at which (1) fusion begins, (2) the fat flows down and obstructs the capillary (Fig. 10*b*), and (3) the completion of fusion is indicated by the entire liquefaction and transparency of the fat.

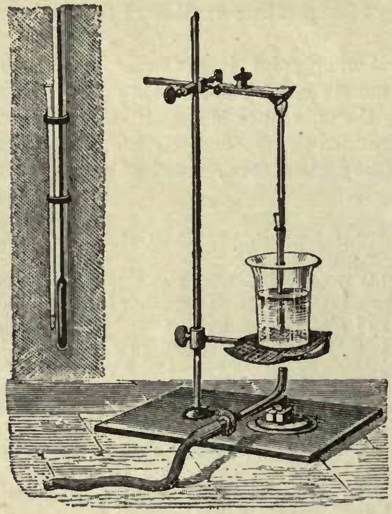

Fig. 9.

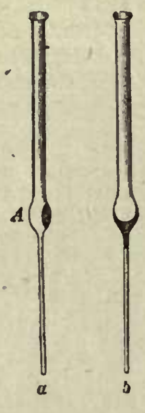

Fig. 10.

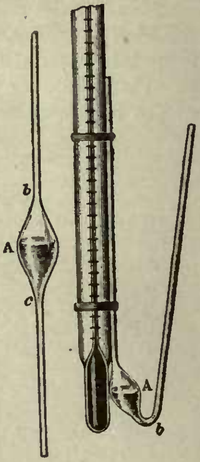

Fig. 11.

The melting-point of a fat may also be determined by drawing it in the fused condition into a capillary tube blown out at the middle into a bulb, which is half filled with the fat (Fig. 11); the upper end of the tube is kept closed with the finger until the fat becomes solid, the empty part of the tube being then bent round as shown and attached, upside down, to a thermometer, the whole being afterwards gradually heated in a beaker of water. When the fat begins to melt it flows into the lower part of the bulb (Fig. 11 *A b*, right-hand view), and when it is completely fused it becomes transparent.

For fats and paraffin waxes, or waxes in general, and for *soft fats* (for example, lubricants) especially, an important determination is that of the *dropping-point*, which is carried out, according to Ubbelohde's method (1905), by filling with the fat a glass capsule, *e* (Fig. 12, natural size), 10 mm. long and 7 mm. wide, with an orifice 3 mm. in diameter in the base; a very small thermometer bulb is immersed in the fat and the capsule then affixed to the thermometer with a metal sheath having an aperture at *c*, and three points, *d*, which

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[1] Exact determinations require correction of the thermometric reading to allow for the cubical expansion of the mercury and glass of that part of the thermometer not immersed in the heated liquid. The observed melting-point, t, is to be increased by $na\,(t - t_1)$, where $n =$ 0·000160 (the mean cubical expansion of mercury in an ordinary glass tube), a is the number of degrees between the surface of the heated liquid and the top of the mercury column and t_1 the air temperature about half-way up the mercury column.

Example: If the indicated melting-point is 80° (t), while the thermometer dips into the liquid as far as the 15° mark, so that $a = 65$ (*i. e.*, 80 — 15), and the temperature half-way up the mercury column is 30° (t_1), the correction becomes $0{\cdot}000160 \times 65 \times (80 - 30) = 0{\cdot}52°$, and the corrected melting-point 80·52°.

determine the position of the capsule; the thermometer is then fixed in a test-tube 4 cm. in diameter, dipping into a beaker of water, which is heated so that the temperature rises one degree per minute. At the orifice of the capsule a drop begins to form at a certain time, and when this falls the temperature is read, and is usually corrected by subtracting 0·5° to obtain the *real* instead of the apparent dropping-point.

This method has been adopted for the examination of lubricating oils supplied to the Italian navy and railways.

The specific gravity of liquids also serves to determine their purity, and the various forms of apparatus used for measuring it are described in Vol. I., p. 75.

ANALYSIS OF ORGANIC SUBSTANCES

As will be seen later, many so-called organic substances are composed of carbon and hydrogen combined in various proportions; a large number of them contain also oxygen, while nitrogen is often present and sometimes sulphur, halogens, metalloids, and metals.

Analysis of these compounds may be merely *qualitative*, when only a knowledge of the constituent elements is required, or it may be *quantitative*, when the percentage amount of each of the elements present is determined.

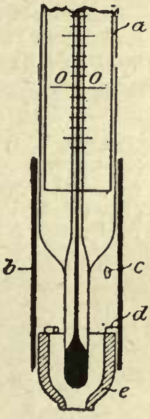

FIG. 12.

QUALITATIVE COMPOSITION. When organic substances are heated on platinum foil they either burn with a flame or leave a carbonaceous residue. The presence of *carbon* and *hydrogen* may be demonstrated by heating a little of the substance, mixed with cupric oxide, in a test-tube fitted with a delivery tube, the gas evolved being passed into a clear solution of barium hydroxide: if the latter becomes turbid, owing to the formation of barium carbonate, the presence of carbon is proved, and if drops of water condense in the cold upper part of the tube the substance must contain hydrogen.

The presence of *nitrogen* may, in many cases, be shown by the smell of burning wool or nails developed when a little of the substance is heated on platinum foil. A more general and certain test is that devised by Lassaigne (1843): 2 to 3 centigrams of the substance are fused with a piece of metallic potassium or sodium (0·2 to 0·3 gram) in a test-tube, which is broken by plunging it while still hot into a beaker containing 10 to 12 c.c. of water. The alkaline solution of potassium cyanide formed is filtered, mixed with a few drops of ferrous sulphate and ferric chloride solutions and boiled for two minutes, by which means potassium ferrous cyanide is formed (when nitrogen is present in the substance); the liquid is acidified with hydrochloric acid, which dissolves the ferrous and ferric oxides, the resulting ferric chloride reacting with the potassium ferrocyanide to form the characteristic Prussian blue, or at least a green solution which deposits Prussian blue on standing. In absence of nitrogen, only a yellow colour is obtained. To certain nitrogenous substances this test is not applicable (*e. g.*, to diazo-compounds, which evolve nitrogen too readily), and in such cases either the potassium is replaced by a mixture of potassium carbonate and powdered magnesium (Castellana, 1904), or the substance is fused with sodium peroxide and the mass tested for nitrate by means of diphenylamine (Vol. I., p. 234). As early as 1825 Faraday detected nitrogen by heating the substance in a tube with caustic soda and soda-lime, the evolution of ammonia being shown by means of litmus paper; spurting of small portions of the soda on to the litmus paper should be prevented by passing the vapour emitted first through a tube containing glass wool (*see later*, Quantitative Determination).

The presence of *halogens* (Cl, Br, I) is determined by heating the substance with *pure* lime, dissolving in water and nitric acid and precipitating the halogen with silver nitrate. Also, in many cases, the substance may be heated with fuming nitric acid and silver nitrate in a sealed tube (*see later*, Quantitative Analysis), by which means the silver halogen salt is formed directly (Carius).

Sulphur also may be detected by the Carius method, the substance being heated in a sealed tube with fuming nitric acid, and the sulphuric acid formed from the sulphur of the organic compound, precipitated with barium chloride; or by heating the substance with pure sodium peroxide, a sulphate is formed. By heating the substance in a test-tube with metallic sodium and dissolving the mass in a little water a solution of sodium sulphide is obtained which blackens a piece of silver foil or a silver coin.

Phosphorus and other elements are detected by the Carius method, the substance being oxidised with fuming nitric acid and the liquid tested for the corresponding acid (phosphoric, etc.).

QUANTITATIVE COMPOSITION (ELEMENTARY ANALYSIS). Lavoisier was the first to devise an apparatus for analysing organic substances by burning them with oxygen under a bell-jar; while Gay-Lussac, Thénard, and Berzelius successively improved this process by burning the substance in presence of potassium chlorate. Gay-Lussac, however, showed that certain nitrogenous substances cannot be burned with the chlorate, and suggested as a general and more certain oxidising agent cupric oxide, which when hot gives up its oxygen, transforming the carbon and hydrogen of any organic compound into carbon dioxide and water respectively, while the nitrous compounds are reduced to free nitrogen by passing the products of combustion over red-hot copper turnings. It is, however, to Liebig that the credit is due of rendering this method of organic analysis simple and exact and of devising simple and ingenious forms of apparatus for absorbing the products of combustion. Even to-day—disregarding improvements in combustion furnaces and modifications of the absorption apparatus—the **determination of carbon and hydrogen** (the oxygen is estimated by difference) is carried out by what is virtually the method employed by Liebig.[1]

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[1] The method most commonly used is as follows : 0·15 to 0·30 gram of the substance is weighed in a small porcelain boat, which is then filled with powdered cupric oxide, previously heated to redness and *perfectly dry* ; the boat is then introduced into the position *c* of the hard glass combustion tube (Fig. 13), this being 70 to 90 cm. long, or 10 to 12 cm. longer than the combustion furnace, which is heated by 25 to 30 gas flames (Fig. 14).

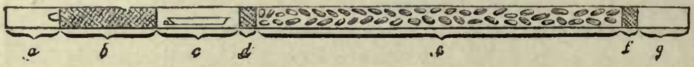

FIG. 13.

a = 5 cm. free; *b* = 12 cm. spiral of oxidised copper gauze; *c* = 8 to 10 cm. for the boat; *d* = 3 cm. copper spiral; *e* = 40 to 45 cm. granulated cupric oxide; *f* = 3 cm. oxidised copper spiral or 12 cm. of reduced copper spiral for nitrogenous substances; *g* = 5 cm. free.

The other parts of the tube are reserved for the previously heated copper spirals and granulated cupric oxide (Fig. 13). When a fresh combustion is to be made, all that it is necessary to do is to remove the spiral *b* and the boat and to introduce the new substance into the tube, which is already charged in *d*, *e*, and *f* and is not allowed to cool below 40° to 60°.

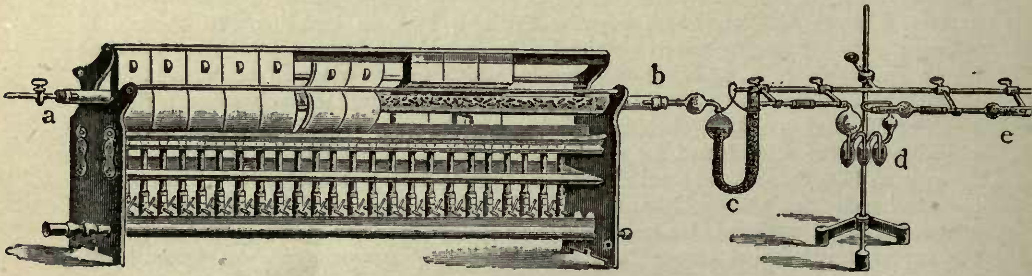

FIG. 14.

The combustion is carried out in the furnace shown in Fig. 14, the tube being closed at *a* with a good cork and a glass tap which can be connected at will with a gasometer containing air or one containing oxygen, which should, however, before reaching the combustion tube, pass through tubes containing potassium hydroxide to remove the carbon dioxide, and then

For determining carbon and hydrogen in *nitrogenous substances* the above method is modified only by inserting in the combustion tube, in place of the spiral *f* (Fig. 13), one of reduced copper gauze[1] about 15 cm. long, this serving to fix the oxygen from the oxides of nitrogen resulting from the combustion and to liberate the nitrogen, which passes unchanged through the absorption apparatus.

If the substance to be analysed contains *sulphur* or a *halogen*, the combustion is made with lead chromate in place of the granular copper oxide, and the heating is more gentle to avoid fusion of the chromate. By this means the sulphur remains fixed in the tube as lead sulphate and the halogens as halogen salts of lead. Halogens may also be fixed on a spiral of silver foil about 10 cm. long placed at *f* (Fig. 13), the substance being combusted as usual with cupric oxide; if both nitrogen and a halogen are present the copper and silver spirals are used together.

A new apparatus, which admits of the combustion of organic substances being very rapidly carried out, has been devised by Carrasco and Plancher (1904–1906).[2]

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through drying tubes containing calcium chloride. At the other end the combustion tube communicates at *b*, first with a tared tube, *c*, containing granulated calcium chloride to absorb the water formed during combustion; then follows the tared apparatus, *d*, containing potassium hydroxide solution (30 to 35 per cent.), which absorbs the carbon dioxide from the burnt substance and is furnished with a calcium chloride tube to retain the moisture given off by the potassium hydroxide solution. Finally follows a calcium chloride tube, *e*, which is not weighed, and prevents moisture entering the apparatus from the air.

Before the combustion is started the apparatus is tested to ascertain if it is perfectly air-tight. This is done by closing the tap *a*, and sucking into *e* eight or ten bubbles of gas; the slight rarefaction produced in the interior of the combustion tube causes the potash solution to rise in the first large bulb to a level which should remain constant for some minutes. The burners at the end *b* are then gradually lighted until the portion *f* and almost all of the portion *e* are heated to redness. The spiral *b* is then gradually heated from the *a* end, the heating being gradually extended under the boat so that the substance is completely burnt. During the combustion bubbles of air are passed into the tube from the gas-holder so as to transport the gases produced into the absorption apparatus; during the last ten to fifteen minutes a gentle current of oxygen is passed through, and then the flames are extinguished and air again passed for ten to fifteen minutes. In this way all the gases from the combustion are removed from the combustion apparatus and the copper oxide is completely reoxidised, so that the tube is ready for the next combustion.

The increases in the weights of the potash and calcium chloride apparatus give the amounts of carbon dioxide and water respectively formed during the combustion, and, since 44 parts of carbon dioxide correspond with 12 parts of carbon and 18 parts of water with 2 of hydrogen, the quantities or percentages of carbon and hydrogen in the substance can be calculated. The sum of these two percentages, when subtracted from 100, gives that of the oxygen, excepting where the substance contains nitrogen, which is determined directly by methods given later. In this way the *percentage composition* is determined.

[1] The reduction is effected in a separate glass tube, through which a current of hydrogen is passed while the spirals are heated; when the copper has assumed its characteristic red colour, the flames are extinguished and the spirals allowed to cool in the current of hydrogen, being afterwards kept in desiccators ready for use; or, better, when reduction is complete and the spirals are still hot, the tube is exhausted and is kept so until cold, so as to avoid the danger of hydrogen remaining occluded by the copper.

[2] It consists of a small external combustion tube, *c* (Fig. 15), of hard glass, and about 20 cm. long and 2 cm. wide, and slightly expanded at the lower closed end. The tube is closed at the top by a rubber stopper, *f*, through which passes a porcelain tube, *e*, wound round with an electric resistance formed of platinum-iridium wire, *d*; along the interior of the porcelain tube passes a thick silver wire, which starts from *d*, the negative pole, and ends in a small platinum wire loop and serves to convey the current (3 amps. at 20 volts). The oxygen for the combustion traverses *OS* and the upright tube of the stand, and passes through the porcelain tube to the bottom of the combustion tube. In the stopper, *f*, is fastened a piece of nickel tube, *b*, which is united to the + pole and to the platinum spiral, *d*, and serves at the same time for the escape of the gases formed by the combustion to the tube *r*. The gases are absorbed by the usual tared apparatus ($u =$ calcium chloride, $p =$ concentrated potassium hydroxide solution), but with nitrogenous or halogenated substances the gases are first passed through a U-tube containing lead dioxide heated to 180° by means of a small furnace, *m*. The connections *a* and *b* are insulated from one another by porcelain and rubber. When the current passes through the resistance the glass tube is heated to redness, and the substance (0·12 to 0·20 gram), mixed with cupric oxide or, better, with platinised porous porcelain powder, and placed at the bottom of the glass tube, is burned by heating the outside of the tube directly with a bunsen flame. The combustion is very soon completed, the platinum-iridium spiral apparently accelerating the oxidation catalytically; apart from the time occupied by the weighings, this method requires fifteen to twenty minutes, and usually gives good results. For the analysis of fairly volatile liquids or of substances which readily sublime, the lower part of the combustion tube is drawn out almost

An electrical method for determining carbon, hydrogen, and sulphur in organic substances was also proposed by Morse and Gray in America in 1906.

QUANTITATIVE DETERMINATION OF NITROGEN. (1) *Dumas' Method.* The nitrogenous organic substance (0·2 to 0·3 gram) is heated in a hard glass tube similar to that shown in Fig. 13, but closed at the end, *a*. The portions *a* and *b* contain sodium hydrogen carbonate or magnesium carbonate; between *b* and *c* is placed a small plug of copper gauze, in *c* granulated copper oxide, and in *d* powdered copper oxide. Then follows a space 10 cm. in length in which is placed the substance to be analysed, this being weighed and mixed with powdered cupric oxide; next comes granulated cupric oxide, and in *f* a spiral of reduced copper, 10 to 12 cm. long.[1]

The extremity, *g*, of the tube is connected by means of a gas delivery tube with a graduated tube (25 or 50 c.c.) placed upside down in a basin of mercury and filled half with mercury and half with concentrated potassium hydroxide solution. This graduated tube may have the form devised by Dumas and shown in Fig. 16; the gas from the combustion tube passes into the tube *a*, furnished with a clip, *m*, thence through a little mercury in the bottom of the tube *b*, which is filled with potassium hydroxide solution and is in communication with a reservoir, *c*, of this solution.[2]

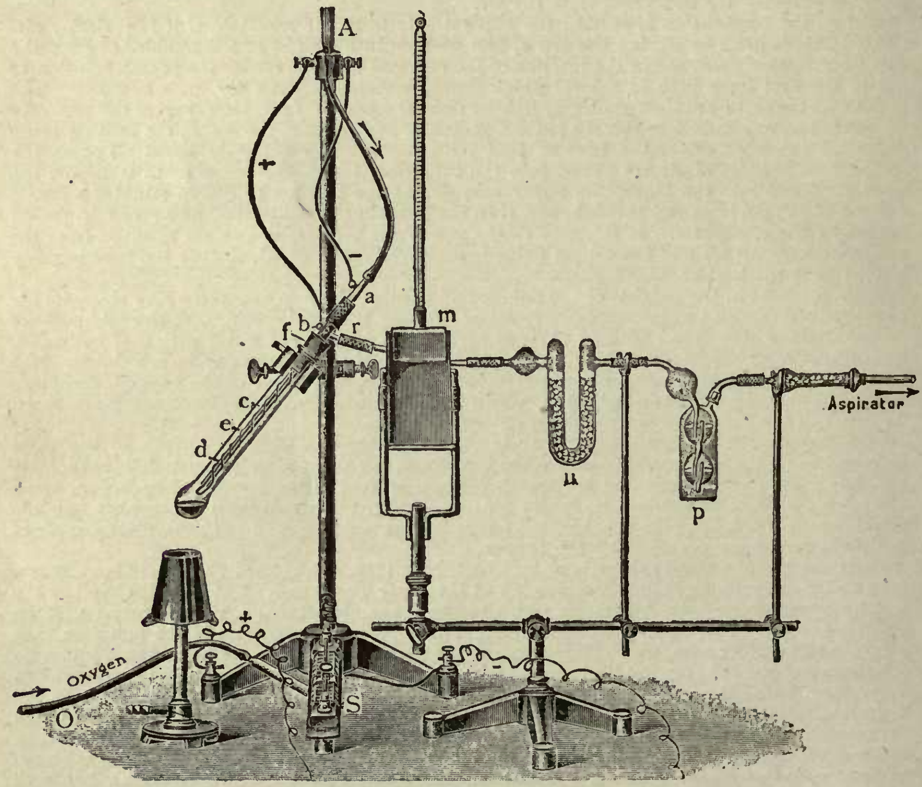

Fig. 15.

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horizontally, and the substance is mixed with platinised porcelain powder (2 to 3 per cent. of platinum); liquids may also be heated in a separate tube and the vapour then injected into the combustion tube.

[1] In this case the copper spiral may be rapidly reduced by heating it over a large non-luminous gas flame and dropping it into a thick-walled test-tube containing $\frac{1}{2}$ c.c. of ethyl or, better, methyl alcohol; the tube is immediately closed by a rubber stopper through which passes a glass tube. The latter is connected with a pump until the spiral is cold.

[2] The operation is begun by heating the combustion tube at the point where the magnesium carbonate lies; the carbon dioxide thus evolved expels the air from the apparatus into *b*, whence it is driven by raising the reservoir, *c*, and opening the cock at the top of *b*. The

When several determinations of nitrogen are to be carried out the procedure is sometimes simplified by using a combustion tube open at both ends, like that of Fig. 13, the magnesium carbonate or sodium bicarbonate being omitted and the combustion tube being connected at *a* with a small Kipp's apparatus for the evolution of carbon dioxide (marble and hydrochloric acid), care being taken to free the apparatus from all air by a prolonged current of carbon dioxide.

(2) *Kjeldahl's Method* (Dyer's modification). 0·5 to 1 gram of the substance is placed in a hard glass flask (200 to 300 c.c.) with a long neck, into which penetrates the stem of a funnel used to cover the flask (Fig. 17). 20 c.c. of concentrated sulphuric acid (66° Bé.) and a drop of mercury (which acts as a catalytic oxidising agent) are added, and the contents of the flask are heated, at first gently and finally more strongly, until vigorous boiling sets in. 10 grams of potassium sulphate are then added, a little at a time, the heating being continued until the liquid is decolorised, by which time the whole of the nitrogen is transformed into ammonium sulphate. After the flask has been allowed to cool, its contents are washed out with water into a flask already containing 200 to 300 c.c. of water. 3 to 4 grams of zinc dust (which decomposes ammoniacal compounds of mercury and prevents bumping by the evolution of hydrogen) are then added, and the flask closed with

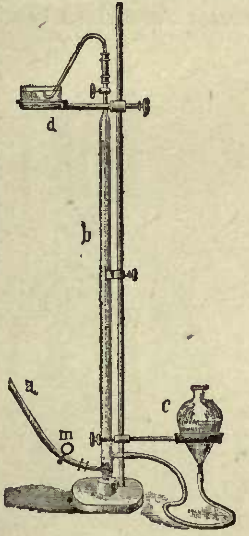

FIG. 16.

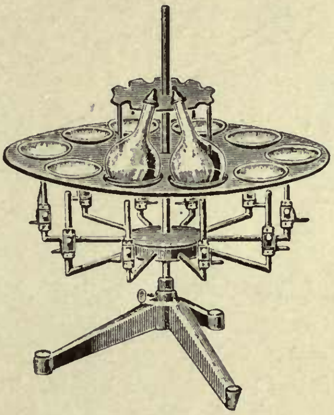

FIG. 17.

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carbon dioxide is absorbed by the potash solution, and when no more air collects in *b* the magnesium carbonate is no longer heated. The copper spiral and the copper oxide are now gradually heated in the same way as for the estimation of carbon and hydrogen, the heating being slowly extended until it reaches the substance itself. Oxides of nitrogen are decomposed by the copper spiral, so that all the nitrogen is evolved in the free state and collects in *b*. Finally the nitrogen remaining in the combustion tube is driven into *b* by means of carbon dioxide formed by again heating the magnesium carbonate.

At the end of the operation, in order to measure the nitrogen, a graduated tube filled with water is inverted over *d*, and the cock at the top of *b* having been opened, the reservoir, *c*, is raised until all the gas passes into the graduated tube. The latter may then be removed to a large cylinder full of water and when, after a few minutes, the gas has assumed the temperature of the water (shown by an accurate thermometer) the tube, grasped by a clip (the hand would warm it), is arranged so that the level of the liquid inside it coincides with that outside, and the volume (v) of the gas read off. At the same time the atmospheric pressure (b) is read, and the exact temperature (t) of the water. The percentage of nitrogen (p) in the substance is then calculated by means of the following formula:

$$p = \frac{v \, . \, (b - w) \, . \, 0{\cdot}12511}{s \, . \, 760(1 + 0{\cdot}00367 \, . \, t)},$$

where s indicates the weight of substance taken, w the pressure of water vapour expressed in mm. of mercury (*see* Vol. I., p. 35), and 0·0012511 gram the weight of 1 c.c. of moist nitrogen at 0° and 760 mm. (Rayleigh and Ramsay).

a rubber stopper through which pass a tapped funnel containing 120 to 160 c.c. of concentrated sodium hydroxide solution (30 to 35 per cent.) and a glass bulb (Figs. 18 and 19) communicating with a simple condensing tube dipping into a flask containing a measured volume of standard sulphuric acid and a drop of methyl orange. In order to prevent spurting of the caustic soda and its introduction into the condenser tube, the glass bulb is fitted with a delivery tube curved towards the wall of the bulb; it is, however, as well to push into this tube, almost as far as the bulb, a small plug of glass-wool or asbestos. Solutions of soda more concentrated than 35 per cent. often lead to spurting. About one-half of the liquid is distilled and the excess of sulphuric acid remaining in the collecting flask determined by titration with alkali. Hence the amount of ammonia fixed by the acid may be calculated and so the percentage of nitrogen in the substance analysed. In Figs. 17 and 19 are shown forms of apparatus with which it is possible to carry out several determinations simultaneously.

Kjeldahl's method cannot be used as it stands for the analysis of organic substances which contain nitrogen either united to oxygen (nitro-compounds) or forming part of a pyridine or similar nucleus (quinoline, etc.). In such cases the method is modified as described under Aromatic nitro-derivatives (Part III).

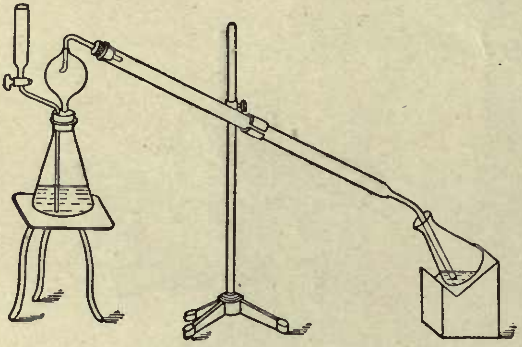
FIG. 18.

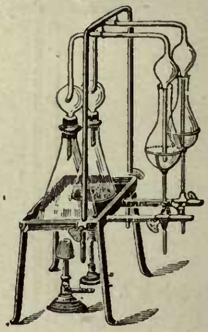
FIG. 19.

(3) *Will and Varrentrapp's Method.* This method is based on the principle that almost all nitrogenous organic substances (which do not contain nitrogen linked to oxygen, such as the nitro-compounds), when they are heated with an alkali hydroxide or, better, with *soda-lime* (*see* Vol. I., p. 618), yield hydrogen, which transforms the nitrogen into ammonia. Little use is made of this method to-day.

QUANTITATIVE DETERMINATION OF THE HALOGENS. The method most commonly used is that of Carius. The substance (0·15 to 0·2 gram) is weighed out in a small tube, which is then introduced into a large, hard glass tube 30 to 40 cm. long and 2 to 3 cm. wide, closed at one end and containing about 2 c.c. of fuming nitric acid and about 0·5 gram of solid silver nitrate; this introduction is effected in such a way that the acid does not enter the small tube. The large tube is then softened near the open end by heating in the blow-pipe flame and gradually drawn out to a point (Fig. 20, *A*), the walls of the tube being allowed to thicken during the fusion (Fig. 20, *B*, shows the upper part of the tube on a larger scale). After being allowed to cool in a vertical position, the tube is introduced into a thick-walled iron sheath, which is closed with a screw-cap. It is then safe to incline the tube and introduce it into a bomb-furnace (Fig. 21), which holds four or more tubes and is raised slightly at one end; this is heated for 4 to 6 hours, the temperature being raised gradually to about 250°. Sometimes the tubes burst owing to the great internal pressure, but without danger from flying fragments of glass owing to the protection of the iron sheaths and of the folding shutters at the ends of the furnace, these being lowered during the heating.

At the end of the operation, when the tube is cool, it is taken from the iron sheath, held in a vertical position, and its point (Fig. 20, *A a*) softened in a bunsen flame. When the pressure in the tube has been thus relieved, a scratch is made with a file at the point marked *b*, and the file-mark touched with a red-hot glass rod, with the result that the upper part of the tube breaks off. The tube is then carefully emptied and washed out into a beaker with water, the small tube, held in pincers or a piece of platinum wire, being well washed inside and outside before removal. The liquid is heated and the precipitated silver halogen compound is then collected on a filter, washed, dried in an oven, detached from the filter and heated in a weighed porcelain crucible until it just begins to melt. After being allowed to cool in a desiccator, the crucible is weighed and the amount of halogen contained in the organic substance calculated from the weight of silver haloid.

QUANTITATIVE DETERMINATION OF SULPHUR AND PHOSPHORUS. This is carried out by the Carius method in the same way as for halogens, except that no silver nitrate is introduced into the tube. At the end of the heating, the sulphur is obtained as sulphuric acid or the phosphorus as phosphoric acid, estimation of the amounts of these acids being effected by the ordinary methods. The halogens, sulphur and phosphorus, may also be determined after fusion of the substance with pure sodium peroxide.

CALCULATION OF THE EMPIRICAL FORMULA. From the results of the elementary analysis of an organic substance may be calculated the *percentage composition*, *i. e.*, the quantity of each component in 100 parts of substance. To deduce the chemical formula, that is, the proportions in which the different atoms enter into the molecule, the percentage weight of each component is divided by the corresponding atomic weight, the numbers thus obtained giving the proportions between the numbers of atoms of the different elements.

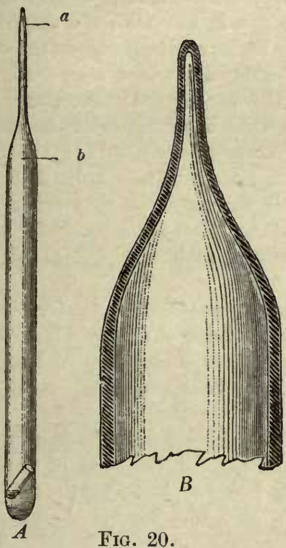

FIG. 20.

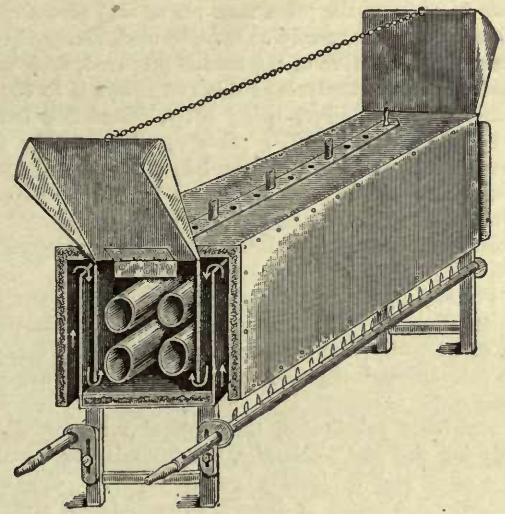

FIG. 21.

These numbers sometimes give directly the numbers of atoms contained in the molecule, but in other cases they represent multiples or submultiples of the real numbers of atoms.

If, for example, *lactic acid* is analysed, the percentage composition is found to be : C, 40 per cent. ; H, 6·6 per cent. ; O, 53·4 per cent. ; by dividing these numbers by the corresponding atomic weights, the following numbers are obtained : C, 3·3 (*i. e.*, $\frac{40}{12}$) ; H, 6·6 ($\frac{6\cdot6}{1}$) ; and O, 3·3($\frac{53\cdot4}{16}$). These proportions have a common factor, 3·3, and division by this gives 1C, 2H, and 1O, *i. e.*, CH_2O, which is an empirical or *minimum formula*, the simplest formula expressing the proportions between the numbers of atoms of the different elements.

This minimum formula does not, however, represent the molecular magnitude, and, in fact, analyses of formaldehyde, acetic acid, grape sugar, etc., give the same percentage composition and the same minimum formula, CH_2O, which must hence be a submultiple of the formulæ of these substances.

A knowledge of the percentage composition is not sufficient to determine the true molecular formula; the molecular magnitude, *i. e.*, the molecular weight, must also be known in order to permit of a choice between the various multiples. By making use of one of the methods described in Vol. I., "Inorganic Chemistry" (pp. 34 *et seq.*), the molecular weight of lactic acid is found to be 90, so that, of the various possible formulæ, CH_2O (mol. wt. 30), $C_2H_4O_2$ (mol. wt. 60), $C_3H_6O_3$ (mol. wt. 90), $C_4H_8O_4$ (mol. wt. 120) . . . . $C_6H_{12}O_6$ (mol. wt. 180), etc., only $C_3H_6O_3$ corresponds with lactic acid. Even this formula and the empirical formula, however, tell nothing concerning the grouping of the atoms in the molecule which, as is explained in the following pages, is given by the constitutional formula.

DETERMINATION OF THE MOLECULAR WEIGHT BY CHEMICAL MEANS

In lactic acid one-sixth of the hydrogen may be substituted by a metal, so that there must be at least six (or a multiple of six) atoms of hydrogen in the acid, the empirical formula being necessarily at least trebled, giving $C_3H_6O_3$. To ascertain if this is the true formula, a derivative of the acid is prepared, such as the silver salt, which may easily be obtained pure. Analysis of this salt shows it to contain 54·8 per cent. of silver, and the atomic weight of silver being 107·7, calculation indicates that the residue of the lactic acid combined with 107·7 parts of silver weighs 89. Assuming that only 1 atom of silver has entered the lactic acid in place of 1 of hydrogen (as may, indeed, be deduced from the fact that the quantity of hydrogen in the salt is five-sixths of that originally present in the acid), the weight of the lactic acid would be $89 + 1$, or 90. The true formula of the acid would hence be that corresponding with a molecular weight of 90, *i. e.*, $C_3H_6O_3$.

For acid substances in general this *chemical method* may be employed for determining the molecular weight, making use of the silver salt and determining if the acid is mono-, di-, or tri-basic (that is, ascertaining if the silver replaces 1, 2, or 3 atoms of hydrogen), the calculation being then based on the presence of 1, 2, or 3 atoms of silver in the salt.

For basic substances, the molecular magnitude may be determined chemically by analysing the *platinichlorides*, the formulæ for which are always of the type of that of ammonium platinichloride: $PtCl_4(NH_3{\cdot}HCl)_2$, the ammonia being replaced by the organic base, which is mono- or di-acid, according as it replaces one or two molecules of ammonia in the platinichloride.

For other (indifferent) organic substances derivatives are prepared by substituting chlorine atoms for one or more hydrogen atoms, the proportion of chlorine being then estimated; the calculation is then similar to that described above.

The *chemical method* for determining the molecular magnitude does not always give certain results: experimental difficulties sometimes occur and often entail great labour. Consequently the determination of molecular weights is usually effected by *physical methods:* vapour density method, cryoscopic method, ebullioscopic method, etc., these being all described and illustrated in Vol. I. (Part I).

POLYMERISM

It sometimes happens that the analysis of different substances shows them to have the same percentage composition, although their chemical and physical properties are different; thus, for example, acetic acid, lactic acid, glucose, etc., contain the same elements, C, H, and O, in the same proportions, there being $2n$ hydrogen atoms and n oxygen atoms for n carbon atoms. Accurate study of these compounds and determination of the molecular magnitude (molecular weight) show that the differences depend on the true formulæ being multiples of the minimum or empirical formula. Thus, whilst the molecule of acetic acid is represented by $C_2H_4O_2$, that of lactic acid corresponds with $C_3H_6O_3$, and that of glucose with $C_6H_{12}O_6$. These molecules are hence all multiples of a hypothetical complex CH_2O, the ratios (but not the absolute quantities) between carbon, hydrogen, and oxygen being the same (1 : 2 : 1) in all cases. These compounds are termed *polymerides* and the phenomenon is known as *polymerism.*

In some instances, however, it happens that the molecular magnitude is not sufficient to differentiate certain compounds, which, besides containing the same elements in the same proportions (equal percentage compositions), have also the same molecular magnitudes, although differing in their physical and chemical properties. To explain the existence of these isomeric compounds, the chemical nature of carbon must be studied more in detail.

VALENCY OF CARBON, ISOMERISM, AND CONSTITUTIONAL FORMULÆ

On the foundation of multivalent radicles,[1] discovered by Odling, and of the investigations of Frankland (1852), which showed that nitrogen,

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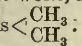
[1] **Theory of Radicles and Types.** In the first twenty years of last century, various compounds were discovered which stood in apparent contradiction to the electro-chemical theory of *dualistic formulæ*, put forward by Berzelius (Vol. I., p. 46); in fact, in certain compounds the hydrogen (electro-positive) was replaced by chlorine (electro-negative) without appreciably changing the chemical characters of the original compounds. It was then that chemical compounds came to be represented by *unitary formulæ*, no account being taken of the grouping of the atoms in the molecule.

Gradually, however, as the number of new organic substances increased, certain analogies became evident in their chemical behaviour. In studying cyanogen Gay-Lussac (1815) had indeed met, in various reactions and in various substances, the residue or radicle CN, which behaved as a monovalent element (like the halogens), combining with one atom of different monovalent metals, etc. In 1832 Liebig and Wöhler discovered and studied a monovalent atomic group or radicle, *benzoyl*, C_7H_5O, which was found in oil of bitter almonds combined with an atom of hydrogen (C_7H_6O); on oxidation by the air, this essence became transformed into benzoic acid, $C_7H_6O_2$, which with PCl_5 gave benzoyl chloride, C_7H_5OCl, and this, in its turn, gave the aldehyde C_7H_6O, when treated with nascent hydrogen, or benzoic acid under the action of water. All these compounds contain the monovalent benzoyl nucleus, C_7H_5O, which passes unchanged from one to the other by combining with monovalent atoms or groups. In 1833, in a classic work, Bunsen studied another radicle, *cacodyl*, which is a monovalent organic arsenic residue,  $As<\begin{matrix}CH_3\\CH_3\end{matrix}$. Later, in 1837, Dumas advanced and developed the *theory of radicles*, studying and classifying organic compounds with reference to the different radicles contained in them, these radicles thus coming to be considered almost as the *elementary substances of organic chemistry.* The condensation of simple radicles leads to a compound radicle, forming a complex which can unite with other atoms or atomic groups. Liebig supported this new theory, whilst Berzelius strenuously opposed it, reproaching Dumas for regarding all chemical combinations as due to reciprocal interchanges of radicles.

Dumas and, still more so, Laurent, as a consequence of the discovery of new substances, arrived logically at the *theory of substitution*, which assumed the possibility of replacing, one by one, the elements forming the radicle or nucleus of certain compounds by other elements or by radicles of other compounds (Dumas termed this phenomenon of substitution *metalepsy*).

Not only the hydrogen and oxygen, but also the carbon of the radicles could, according to Laurent, be replaced by other radicles or other elements, *e. g.*, by chlorine, without the fundamental characters of the original substances being substantially changed.

These last consequences of the *theory of substitution in radicles* (Dumas) or in nuclei (Laurent) were combated not only by Berzelius, but even by Liebig, who attempted to cover these new conceptions with ridicule and published in his "Annalen" (1840) a pungent satire in the form of a letter from Paris which was signed "S. C. H. Windler" (*Schwindler* being the German for swindler!), and which made the astonishing statement that it had been found possible to replace all the atoms of the molecule of manganese acetate by the corresponding number of chlorine atoms, the resulting substance retaining the characters of the original salt, although formed of chlorine alone; further, on the basis of the new theory, it was concluded that the chlorine used in England to bleach textiles replaced the hydrogen, oxygen, and carbon, and that already chlorine was being spun for the manufacture of nightcaps, which were greatly appreciated!!

Nevertheless, the new conceptions triumphed with the aid of numerous discoveries, which served to confirm, more and more, the ideas of Laurent and Dumas. Moreover, with the studies of Gerhardt, new horizons were opened to organic chemistry, which for so many years found a solid basis in Laurent and Gerhardt's (1852) *theory of types*, this clearing up the nebulous ideas then still held on the atom and the molecule, and it is due to these two investigators that phosphorus, and other elements easily form compounds with three or five equivalents of other elements, Kekulé, in 1857 and 1858, accurately developed the true conception of *valency*, showing the constant tetravalency of carbon and thus widening the horizon of organic chemistry and originating the remarkable theoretical and practical development of the past half-century.

Kekulé and, independently of him, Cooper brought to light another most important property of carbon, resulting from its four equivalent valencies; they showed that carbon atoms possess also the property of combining directly one with another, in a greater or less number, mutually saturating one, two, or even three valencies and forming varying chemical compounds. For convenience, we represent these compounds graphically, placing the carbon atoms in an open or closed chain and saturating the valencies remaining free with other elements (usually hydrogen and oxygen). We have thus a series of groups differing according as the atoms united in a chain are few or many (even more than 30), according to whether the chain is branched by means of lateral chains, and also according as the valencies saturated between carbon and carbon are 1, 2, or 3.

If we represent the valencies of carbon by strokes, the valencies of the different carbon atom chains are given by the numbers of free valencies which are not used in uniting the

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Avogadro's work, denied by everybody, finally assumed the important position accorded to it in modern chemistry.

All organic and inorganic compounds were explained by comparing them with simple types of inorganic substances of well-known constitutions. The fundamental types of Gerhardt were four in number: $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}$, $\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}$, $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$, $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$.

It was supposed that all the principal chemical compounds then known were derived from these types by simple substitution of the hydrogen by other elements and radicles. From the first type may be derived, for example: hydrocyanic acid, $\left.\begin{matrix}\mathrm{CN}\\\mathrm{H}\end{matrix}\right\}$; ethane, $\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{H}\end{matrix}\right\}$; ethyl cyanide, $\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{CN}\end{matrix}\right\}$, etc.; from the second, sodium chloride, $\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}$; ethyl chloride, $\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{Cl}\end{matrix}\right\}$; acetyl chloride, $\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{Cl}\end{matrix}\right\}$; and so on. With the third type correspond, for example, sodium hydroxide, $\left.\begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$; nitric acid, $\left.\begin{matrix}\mathrm{NO_2}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$; acetic acid, $\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$; nitric anhydride, $\left.\begin{matrix}\mathrm{NO_2}\\\mathrm{NO_2}\end{matrix}\right\}\mathrm{O}$; acetic anhydride, $\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{C_2H_3O}\end{matrix}\right\}\mathrm{O}$, etc.

From the fourth type, Hofmann and Wurtz deduced theoretically and prepared in the laboratory a large number of compounds, part or all of the hydrogen atoms of ammonia being replaced; for example, ethylamine, $\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$; diethylamine, $\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{C_2H_5}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$; trimethylamine, $\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\right\}\mathrm{N}$; acetamide, $\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$, etc.

To explain the existence of polybasic acids and various other substances, Odling, Williamson, and Kekulé had recourse to the idea of *multiple types*, sulphuric acid being regarded as derived from the double water type, $\begin{matrix}\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\\\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\end{matrix}$, thus $\left.\begin{matrix}\mathrm{H}\\\mathrm{SO_2}\\\mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}$, and similarly succinic acid, $\left.\begin{matrix}\mathrm{H}\\\mathrm{C_4H_4O_2}\\\mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}$, etc.; for glycerol a triple type was assumed, and so on.

In 1856 Kekulé introduced another very important type, that of marsh gas, $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{C}$, with tetravalent carbon, to which he referred numerous organic compounds; also certain compounds may be referred both to marsh gas and to ammonia, for example, methylamine, $\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$, or $\left.\begin{matrix}\mathrm{NH_2}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{C}$, and from these different methods of considering the constitution and the reference to different types, were deduced various processes for preparing one and the same compound from different starting materials.

carbon atoms among themselves and which can be saturated by different elements (usually H, O, N), giving rise to an enormous number of organic compounds.[1]

The physical and chemical differences of these compounds, termed isomerides, are explained by the different grouping or linking of the atoms in the molecule. *In their chemical transformations, isomerides give up or exchange quite different atomic groups or atoms*, owing to the different functions and positions occupied by these atoms or groups in the molecule.

The first cases of isomerism were discovered by Berzelius in 1833 during an investigation of racemic acid.

It is hence not sufficient to represent organic compounds by an empirical molecular formula, the **structural or constitutional formula**, deducible from the graphic representation of the chains illustrated above, being necessary in many cases to distinguish between isomerides.

To decide which of two isomeric formulæ should be assigned to a given substance, various chemical reactions are carried out with the substance, study of the resultant new products indicating the constitutional formula.[2]

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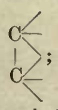
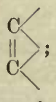
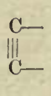
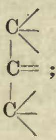
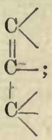
[1] The following are some of these hypothetical carbon atom chains:

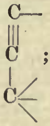
(1)  ;
Hexavalent

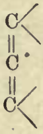
(2)  ;
Tetravalent

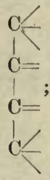
(3)  ;
Divalent

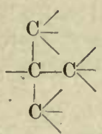
(4)  ;

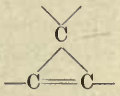
(5)  ;

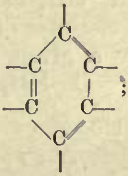
(6)  ;

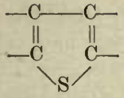
(7)  ;

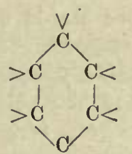
(8)  ;

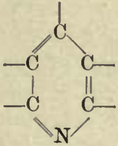
(9)  , etc.

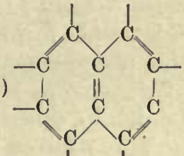
(10)  ;

(11)  ;

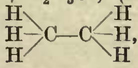
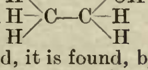
(12)  ;

(13)  ;

(14)  ;

(15) 

Among these chains are two (Nos. 8 and 9) containing four carbon atoms and having equal numbers of free valencies. By saturating these ten free valencies with ten H atoms two compounds are obtained (these have actually been prepared) which contain equal numbers of C and H atoms, and have therefore the same percentage composition and the same molecular weight.

[2] An example will render these ideas clear: It is found that *ethyl alcohol* (ordinary liquid alcohol) and gaseous *methyl ether* have different physical and chemical properties, although they possess the same percentage composition and the same molecular magnitude, represented by the formula C_2H_6O. The constitutions or internal molecular structures of the two compounds are determined by a study of the following chemical reactions: treatment of the alcohol with hydrochloric acid gives first a compound C_2H_5Cl (ethyl chloride), one atom of monovalent chlorine having replaced one atom of oxygen and one of hydrogen or a hydroxyl residue, OH. By means of nascent hydrogen, the chlorine atom of ethyl chloride may be replaced by a hydrogen atom, giving the compound C_2H_6 (ethane). These reactions are hence expressed by the following equations: (1) $C_2H_5 \cdot OH + HCl = H_2O + C_2H_5Cl$; (2) $C_2H_5Cl + H_2 = HCl + C_2H_6$; ethane, however, can have only the constitution,  $H_3 \!>\! C{-}C \!<\! H_3$, *i. e.*, $CH_3{-}CH_3$, so that the alcohol will have the constitution  $H_3 \!>\! C{-}C \!<\! (OH)H_2$

On the other hand, it is found, by various reactions, that the six hydrogen atoms of methyl ether present no difference one from another, and, no matter under what conditions hydriodic acid acts on the ether, it eliminates the oxygen as water, and another product is obtained which contains only one carbon atom in the molecule: The reaction hence takes place according to the equation:

$$C_2H_6O + 2HI = 2CH_3I + H_2O.$$

It is evident, then, that in methyl ether the six hydrogen atoms are united homogeneously

Use is not always made of constitutional formulæ, since they are not simple and are often inconvenient to write; hence attempts are made to simplify them by indicating the more important groups or residues contained in the molecule and giving at the same time an idea of the constitutions and of the functions of these groups; this is done by means of the so-called *rational formulæ*. The rational formula of ethyl alcohol will be $C_2H_5 \cdot OH$, in which the monovalent OH residue, characteristic of all the alcohols, is separated; that of acetic acid will be $CH_3 \cdot COOH$, the group COOH being characteristic of, and common to, all organic acids, etc.

METAMERISM. Constitutional and rational formulæ explain clearly isomerism in general and also the special case bearing the name *metamerism.* When, to an atom of a polyvalent element are united one or more groups in their different isomeric forms, we have special cases of isomerism for definite groups of substances.[1]

PSEUDOISOMERISM, TAUTOMERISM, DESMOTROPY. A substance sometimes contains atomic groups that occupy a very precarious (labile) position, since they exert certain influences one on the other and under given conditions may react in different ways, giving now one new substance and now another; this explains how it is that some compounds having a well-defined chemical character may, under some conditions, behave like substances with other chemical characters, without it being necessary to assume a true change of constitution. Thus, for example, some of the derivatives of cyanic acid, $CN \cdot OH$, behave like derivatives, sometimes of the formula $N \equiv C—OH$ and sometimes of the formula $NH = C = O$, when the hydrogen atom is replaced by a given radicle. The same is the case for derivatives of cyanamide, $N \equiv C—NH_2$, and of carbodiimide, $NH = C = NH$, and of the two non-nitrogenous types, $-C(OH) = \overset{|}{C} - CO -$ and $- CO - \overset{|}{C}H - CO -$, where a hydrogen atom oscillates between the two carbon atoms. These compounds exist usually in only one form, the more stable one, but in the derivatives this stable form, simply on heating, is transformed into the labile one. For this phenomenon Baeyer proposed the name *pseudoisomerism*, and others that of *desmotropy;* it may be assumed that the other isomeride is present in minimal quantity, not detectable by ordinary reagents.

These forms may be distinguished sometimes by chemical reactions, but more generally by the molecular refraction, dielectric constant, magnetic rotation, electrical conductivity, etc. (Under the heading Ethyl acetoacetate, Knorr and Meyer's method for separating the two forms is described.)

In various substances, where several hydroxyls are present in more or less

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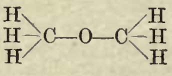
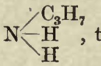
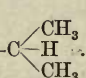
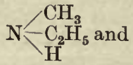
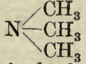
to the two atoms of carbon and that the carbon atoms are joined, not directly, but indirectly, by means of an oxygen atom, which is readily eliminated. The constitutional formula of methyl ether will hence be:

 or $CH_3—O—CH_3$.

[1] For example, in the compound,  $N \begin{cases} C_3H_7 \\ H \\ H \end{cases}$, the monovalent group $—C_3H_7$ may be present in its isomeric forms, *i. e.*, either as $—CH_2—CH_2—CH_3$ or as  $—C \begin{cases} CH_3 \\ H \\ CH_3 \end{cases}$. Although there is considerable resemblance between these two compounds, their different constitutions are manifested in certain chemical and physical properties. The following compounds are also *metameric isomerides:*  $N \begin{cases} CH_3 \\ C_2H_5 \\ H \end{cases}$ and  $N \begin{cases} CH_3 \\ CH_3 \\ CH_3 \end{cases}$; in fact, although the percentage compositions and molecular magnitudes are the same in both cases, the substituent groups of the ammonia molecule are different and the compounds belong to different categories—disubstituted and trisubstituted ammonias.

adjacent positions, there is often a tendency for intramolecular transformation to take place with condensation of two of these groups and separation of a molecule of water, giving rise to isomeric anhydrides, ethers, ketones, or alcohols, etc. In their turn, these derivatives or isomerides, which may be transformed one into the other, give rise to distinct classes of compounds; this isomerism is called tautomerism, and may be regarded as *dynamic* rather than *static* isomerism.

STEREOISOMERISM OR ISOMERISM IN SPACE. We have already seen that, by the tetravalency of carbon and its property of uniting with itself to form various chains, it is possible, in certain cases, to explain the existence of isomerides, which have the same percentage composition and molecular magnitude, but different groupings within the molecules. Many cases of isomerism, foreseen from theoretical considerations, have since been actually met with and different isomerides have been prepared artificially after their existence had been foretold.

For a long time, however, certain compounds were known for which ordinary isomerism did not provide any explanation; among these the most important, from an historical point of view also, are the four dihydroxysuccinic acids (*tartaric acids*), of which two (ordinary tartaric acid and racemic acid) were studied by Berzelius as long ago as 1830. To these must be added lævo-rotatory tartaric acid and mesotartaric acid, discovered by Pasteur. All these compounds have the same internal grouping of the atoms, although they are isomerides; it is not possible to distinguish between them by chemical reactions, but they may be clearly differentiated by their physical behaviour: they form *hemihedral*, *i. e.*, symmetrical, but non-superposable crystals (related as an object to its image in a mirror): they have, too, different actions on polarised light, the plane of which is turned to the right by some and to the left by others. These acids are hence known as *physical* or *optical isomerides.*

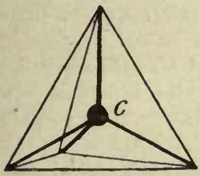


FIG. 22.

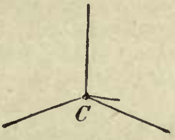


FIG. 23.

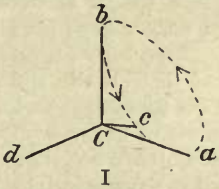


FIG. 24.

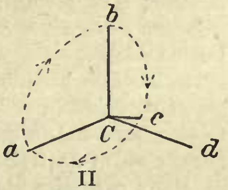


FIG. 25.

Pasteur attempted to explain this isomerism by supposing the atomic groups to be arranged unsymmetrically in the molecule, in some cases in a dextro-rotatory spiral and in others in a lævo-rotatory spiral, or arranged at the *vertices of an irregular tetrahedron.*

When other similar isomerides—the lactic acids—had been discovered, J. Wislicenus, in 1873, suggested that isomerism of this kind could be explained only by *regarding the groups or atoms of these compounds as arranged in space so as to form distinct configurations.*

This isomerism in space (*stereoisomerism*) was explained by van 't Hoff and Le Bel (1874), independently, by means of the hypothesis of the *asymmetric carbon atom.* The starting-point of this hypothesis was Kekulé's idea (1867) of regarding, for the sake of convenience, the carbon atom as situated at the centre of a regular tetrahedron, and its four affinities as directed towards the four vertices, *i. e.*, arranged homogeneously in space (Figs. 22, 23). If these affinities are satisfied at the vertices by monovalent atoms or atomic groups, the following cases present themselves: no isomerism is possible in the compounds $Ca_3\,b$, $Ca_2\,b_2$, $Ca_2\,bc$, and $Ca\,b_2\,c$, where a, b, and c indicate either atoms other than carbon or groups of atoms (I, H, OH, etc.); the compound CH_2I_2 exists in only one form, and if we put the four atoms (H_2 and I_2) at the apices of the carbon tetrahedron, no matter how their positions may be changed, it is not possible to find two different, *i. e.*, non-superposable, arrangements. If, however, the four groups or atoms combined with the carbon atom are all different, *e. g.*, *Cabcd*, two isomerides are possible, and in this case the carbon atom is termed *asymmetric;* in fact, if these atoms or groups are arranged, in one case, so that the circle *a*, *b*, *c* has a sense opposite to that in which the hands of a clock move (Fig. 24, I) (called, therefore, *dextro-rotatory isomerides*, and indicated by *d-* or by the sign +) and, in the other, in the opposite sense (Fig. 25, II) (termed *lævo-rotatory* *isomerides,* like levulose, and indicated by *l*- or —), two non-congruent configurations are obtained; these cannot be superposed, one on the other, in such a way that the same groups occupy the same positions in the two cases. These two figures represent two different isomerides and are related in the same way as an object to its mirror-image or as the left hand to the right. Such isomerism is called *enantiomorphism.*

These two different arrangements of the atoms round the asymmetric carbon atom also explain how it is that, when polarised light traverses these molecules, its plane of polarisation is rotated, in one case to the right and in the other to the left. Van 't Hoff and Le Bel pushed their deductions still further, and showed that the dextro-optical deviation should be numerically equal to the lævo-optical deviation of the corresponding isomeride. This has been confirmed practically, and it also follows that when a pair of such isomerides are mixed in equal proportions, there should result an optically neutral mixture, thus giving rise to a special inactive or *racemic* isomeride. *A substance with only one asymmetric carbon atom always gives three stereoisomerides* (for example, three lactic acids).

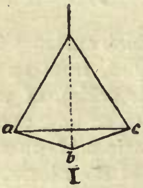


FIG. 26.

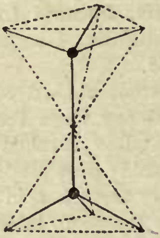


FIG. 27.

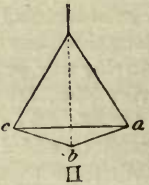


FIG. 28.

It has also been deduced theoretically and proved practically that *all optically active compounds contain at least one asymmetric carbon atom,*[1] although not all compounds containing asymmetric carbon atoms are optically active, since the molecules may contain groups which neutralise each other's activity.

Many examples illustrating these principles will be discussed later in the special part of this book; meanwhile mention may be made of the most important of these compounds: *leucine, asparagine, coniine,* the *lactic acids* (hydroxypropionic acids), etc., which contain one asymmetric carbon atom and give, in each case, three *stereoisomerides.*

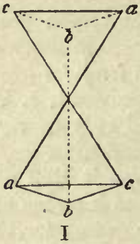


FIG. 29.

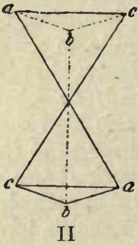


FIG. 30.

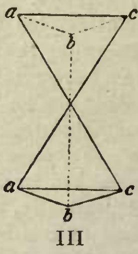


FIG. 31.

These cases of stereoisomerism, and those which follow, will be understood more easily if studied by means of cardboard tetrahedra with differently coloured vertices.

When the substance contains two asymmetric carbon atoms, the number of stereoisomerides increases as follows:

If we take two tetrahedra like that shown in Fig. 26, I, or Fig. 28, II, representing two similar molecules which contain only one asymmetric carbon atom and in which the groups *a*, *b*, and *c*, satisfying three of the valencies, are arranged in a dextro-rotatory sense, and

---

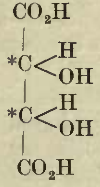
[1] Or else an asymmetric atom of nitrogen (*see later*) or sulphur, tin, etc. The exceptions to this rule are very rare and uncertain, one of the cases most discussed during recent times (1909–1910) being 1-*methylcyclohexylidene*-4-*acetic acid,* which does not appear to contain an asymmetric carbon atom, but is optically active.

superpose one tetrahedron on the other, so that the free valencies satisfy one another, there results a new isomeride, *i.e.*, a molecule with two dextro-rotatory asymmetric carbon atoms, as shown in Figs. 27 and 29.[1]

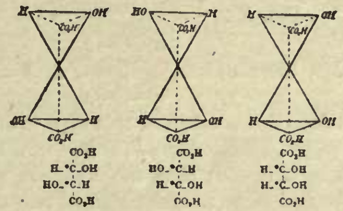
If we join two lævo-rotatory carbon atoms (Fig. 28, II), that is, the mirror image of Fig. 26, I, a lævo-rotatory isomeride (Fig. 30, II) is obtained.

Finally, if one dextro-rotatory (Fig. 26, I) and one lævo-rotatory asymmetric carbon atom (Fig. 28, II) are united, a third stereoisomeride is obtained, which is permanently optically inactive (Fig. 31, III), the effect produced on polarised light by one asymmetric carbon atom being destroyed by the effect of the other.

In order to understand these stereochemical speculations better, we may apply them to the isomerism of *tartaric acid*, which has the formula $C_4H_6O_6$, and contains two asymmetric carbon atoms (marked with asterisks) to which are joined the groups OH, CO_2H, and H :



$$\begin{array}{l} CO_2H \\ \;| \\ {}^*C{<}^{H}_{OH} \\ \;| \\ {}^*C{<}^{H}_{OH} \\ \;| \\ CO_2H \end{array}$$



I II III

FIG. 32.

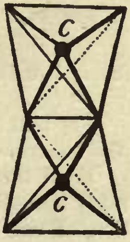


FIG. 33.

If, for the letters *a*, *b*, and *c* of the tetrahedra considered above, we substitute the groups OH, CO_2H, and H, and if the tetrahedron of Fig. 26, I (which we shall call $+A$) be represented as if projected on to a plane, thus: $\begin{array}{ccc} & | & \\ a— & C & —c \\ \searrow & | & \\ & b & \end{array}$ or $\begin{array}{ccc} & | & \\ OH— & C & —H \\ \searrow & | & \\ & CO_2H & \end{array}$ (dextro-rotatory), and that of Fig. 28, II ($-A$), thus: $\begin{array}{ccc} & | & \\ c— & C & —a \\ & | & \swarrow \\ & b & \end{array}$ or $\begin{array}{ccc} & | & \\ H— & C & —OH \\ & | & \swarrow \\ & CO_2H & \end{array}$ (lævo-rotatory), we arrive at the following stereoisomerides of tartaric acid :

I. By joining two $+A$ atoms, we get *d*-tartaric acid (Fig. 29 or 32, I).

II. By joining two $-A$ atoms, we get *l*-tartaric acid (Fig. 30 or 32, II).

III. By joining one $+A$ atom with one $-A$ atom, we have the permanently inactive mesotartaric acid (*i*-tartaric acid), as may be seen in Fig. 31, III, or 32, III.

IV. By mixing, mechanically, equal parts of acids I (+) and II (−), there results *racemic acid*, apparently inactive, but from which, by mechanical means (by hand with the aid of a lens), the two forms of crystals may be separated.

It is often assumed that the two asymmetric carbon atoms can rotate independently on the common axis joining them, so that if the groups of one asymmetric carbon atom exert an attraction or influence on those of the other, a most *favourable position* could be attained, a chemical reaction being sometimes possible between one group and another with separation of, say, water and loss of the freedom of rotation; to the new isomerism thus created we shall refer shortly.

STEREOISOMERISM IN DERIVATIVES WITH DOUBLY LINKED CARBON (ALLOISOMERISM). By means of the tetrahedra, we can show a double linking between two carbon atoms by arranging one side of one tetrahedron (carbon atom) in contact with a side of the other (Fig. 33).

With such an arrangement, even without asymmetric carbon atoms, isomerism is possible. In fact, a compound ${}^{a}_{b}{>}C=C{<}^{a}_{b}$ forms the following isomerides: (1) that shown in Fig. 34, where the two similar atoms or groups of atoms, *e. g.*, *a* and *a*, although

---

[1] Looking at the order in which the letters *a*, *b*, and *c* come in the two asymmetric carbon atoms, it would seem that these are not dextro-rotatory, but this is because the upper carbon atom has been turned through 180° from its position in Fig. 26; if its base is brought down, its identity with the other dextro-rotatory atom becomes evident.

united to two different carbon atoms, occupy adjacent positions: $\begin{array}{c}a\text{—C—}b\\ \Vert\\ a\text{—C—}b\end{array}$, or *cis*-positions (*cis-isomerism*); such a molecule exhibits *plane-symmetry*, the two pairs of similar groups lying to the left and right, respectively, of the perpendicular plane containing the common side (double linking); (2) that shown in Fig. 35, where two similar groups occupy non-adjacent or diagonally opposite or *trans*-positions $\begin{array}{c}a\text{—C—}b\\ \Vert\\ b\text{—C—}a\end{array}$, this form exhibiting *centro-symmetry.*

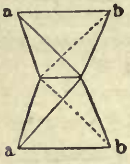


FIG. 34.

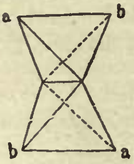


FIG. 35.

Similarly, a compound of the type ${}^{a}_{c}\!>\!C=C\!<\!{}^{a}_{b}$ forms two isomerides, the *cis*-form, $\begin{array}{c}a\text{—C—}b\\ \Vert\\ a\text{—C—}c\end{array}$, and the *trans*-form, $\begin{array}{c}a\text{—C—}b\\ \Vert\\ c\text{—C—}a\end{array}$.

The best illustration of isomerism of this type is afforded by the two isomerides: *maleic acid* (*cis*-form, Fig. 36) and *fumaric acid* (*trans*-form, Fig. 37).

From these figures it is seen that the *cis*-form, maleic acid, should lend itself to the ready formation of *anhydrides* (condensation of two molecules or acid groups with separation of one molecule of water), since the two acid groups, CO_2H, are very near to one another, and it is, indeed, found that maleic acid easily gives an anhydride with separation of one molecule of water (Fig. 38), whilst no anhydride of fumaric acid is known.

Isomerism of this kind is exhibited by various substances, *e. g.*, *crotonic* and *isocrotonic acids* ($CH_3 \cdot CH : CH \cdot COOH$); *mesaconic* and *citraconic acids* [$CH_3 \cdot C(COOH) : CH \cdot COOH$], etc.

Baeyer found that cases of isomerism similar to those just described occur also with *cyclic* compounds (*see* Part III), *i. e.*, closed-chain compounds with simple linkings between the carbon atoms. He distinguishes with the sign Γ compounds containing true asymmetric carbon (*absolute asymmetry*), adding the sign + or — if the compound is optically active; while he gives the name *relative asymmetry* to that shown by compounds with doubly linked carbon atoms (*alloisomerism*) or by cyclic compounds with simple linkings, the term *cis* or *trans* being added to the Γ. Thus, to the name tartaric acid would be added the sign $\Gamma +$ or $\Gamma -$, according as the acid is dextro- or lævo-rotatory, and to the name maleic acid Γ^{cis}, to fumaric acid Γ^{trans}, etc.

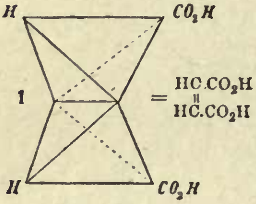


FIG. 36.

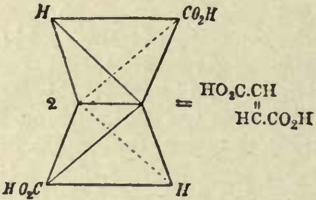


FIG. 37.

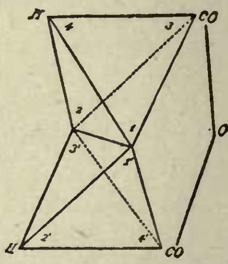


FIG. 38.

STEREOISOMERISM OF NITROGEN. Le Bel attempted to explain the isomerism of certain nitrogen compounds (*e. g.*, methyl-ethyl-propyl-isobutyl-ammonium chloride) by assuming *absolute asymmetry* for the nitrogen atom. A more plausible explanation seems, however, to be afforded by the idea of *relative asymmetry* of the nitrogen, analogous to that of carbon atoms when united by double linking; in this way V. Meyer, Hantzsch, Werner, and others easily explained the isomerism of the oximes, hydroxamic acids, phenylhydrazones, etc. In general, a substance of the constitution $\begin{array}{l}\mathrm{C}\,a\,b\\ \Vert\\ \mathrm{N}\,c\end{array}$ should give two isomerides, which may be represented as shown in Fig. 39: the *syn*-series (Fig. 39, I) and the *anti*-series (Fig. 39, II).

These investigators also studied those cases of isomerism in which the nitrogen behaves as a pentavalent element.

Of interest are the complex cases of stereoisomerism exhibited by the organic cobalt derivatives studied by Werner (1911–1914) (*see* Vol. I., p. 848).

SEPARATION AND TRANSFORMATION OF STEREOISOMERIDES. Stereoisomerides and, in general, compounds containing asymmetric carbon atoms, when prepared artificially in the laboratory from inactive substances, are inactive, the *racemic configuration*, composed of a mixture of the *optical antipodes* in equal quantities, being formed. When, however, these substances are elaborated in the animal or vegetable organism, they are usually optically active.

The transformation of one of these optical antipodes into the other corresponding with it may sometimes be effected by passing through halogen derivatives, separation of the halogen from which results in the formation of the isomeride of opposite optical activity.

The separation of the antipodes, or of one of them, from the racemic isomeride was carried out by Pasteur (1848) in various ways. The following are the methods used at the present time:

(1) By fractional crystallisation (*see above*) of the racemic isomerides or of some of their salts at various temperatures and from various solvents, the antipodes may be separated directly or else they crystallise in hemihedral forms which may be readily separated. For some substances it is convenient to prepare compounds with alkaloids (optically active basic compounds, *e. g.*, strychnine, cinchonine, etc.), which, even when they do not form well-defined hemihedral crystals, may be easily separated by fractional crystallisation.

(2) By means of *enzyme* action (maltase, emulsin, etc.; *see* section on Fermentation) Fischer succeeded in resolving certain racemic glucosides. Much earlier than this, Pasteur discovered that certain bacteria or moulds (*Penicillium glaucum*, etc.) are capable of developing in a solution of the racemic substance at the expense of one of the optical antipodes, the other being left unchanged. This phenomenon is explained by the fact that bacteria owe their activity to certain substances which they produce (enzymes), and which are optically active and behave analogously to optically active solvents. Indeed, in many cases, stereoisomeric antipodes are separated by virtue of their different solubilities in an optically active solvent.

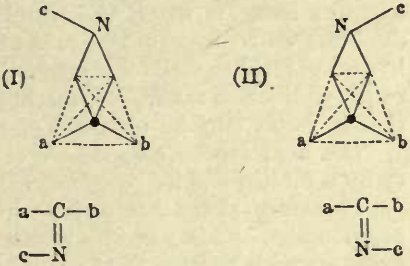


FIG. 39.

(3) With certain racemic compounds, the antipodes are separated by taking advantage of their different *velocities* of *esterification* in presence of an optically active alcohol; *e. g.*, for racemic mandelic acid, menthol (which is an active alcohol) is used. For inactive alcohols the velocity of esterification is the same for the two antipodes composing the racemic compound.

(4) When an optically active substance is heated within certain definite limits of temperature (*transformation point*, *see* Vol. I., p. 208), it is often converted, to the extent of one-half, into the oppositely active isomeride, so that an inactive mixture (racemic compound) is obtained; this takes place readily, for example, with the lactic acids. Above the transformation point the racemic substance may form inseparable *mixed crystals* (*see* Vol. I., p. 116), the substance being then called *pseudo-racemic*. On the other hand, it has been shown that, with certain halogenated compounds, the transformation occurs even at ordinary temperatures, but with a minimum velocity; thus, with isobutyl bromopropionate, about three years is required.

(5) R. Stoermer (1909 and 1911) found that the more stable form with the higher melting-point is often converted into the more labile form by means of the ultra-violet rays (mercury vapour lamp, *see* Vol. I., pp. 238, 687), this occurring especially with ethylene compounds (crotonic acid forms an exception); in this way it is shown that cumarinic acid is the *cis*-alloisomeride of *o*-cumaric acid. The light acts as a source of energy and the *cis*-alloisomerides are the forms containing the most energy. In many cases these alloisomerides cannot be obtained by other methods; when left, they undergo gradual transformation into the more stable isomerides.

HOMOLOGY AND ISOLOGY

Turning to the more simple compounds, those formed from only carbon and hydrogen, we may easily see what procedure is necessary to arrive at those containing longer and more complex chains of carbon atoms. If we start from the most simple compound, *methane* (or marsh gas), CH_4, we may replace an atom of hydrogen in it by other elements or even condense two of the monovalent CH_3 residues into one compound, $CH_3 \cdot CH_3$, thus obtaining *ethane* (C_2H_6). Further, in this compound we may also replace an atom of hydrogen by another $—CH_3$ residue, forming *propane*, $CH_3—CH_2—CH_3$ or C_3H_8, and by continuing this process we arrive at *butane*, $CH_3—CH_2—CH_2—CH_3$, *i. e.*, C_4H_{10}; *pentane*, C_5H_{12}; *hexane*, C_6H_{14}, etc.

All the compounds of this series have analogous structures and have also many analogous chemical and physical properties; such a series is called a *homologous series.*

This series of the derivatives of methane may be represented by the general formula C_nH_{2n+2}, each term being the higher or lower homologue of the preceding or following term, and differing from it by having one CH_2 complex more or less. If in all the simple compounds of this homologous series of methane we replace successively one hydrogen atom of the CH_3 group by the hydroxyl residue OH (characteristic of the alcohols), we obtain a homologous series of alcohols: CH_3OH, methyl alcohol; C_2H_5OH, ethyl alcohol, etc., and similar series may be obtained of aldehydes, acids, chloro-derivatives, etc.

The homologous compounds of each of these series differ always by CH_2 or by a multiple of it.

There are also other series with chains containing double linkings, (*i. e.*, compounds not completely saturated), and these unsaturated series are termed *isologous* with respect to the first, and, for an equal number of carbon atoms, they contain less hydrogen (C_nH_{2n} or even C_nH_{2n-2}).

Thus, ethane is isologous to the two-carbon-atom compounds of the unsaturated series, $CH_2=CH_2$ (ethylene) and $CH\equiv CH$ (acetylene), etc.

Homology is determined by the tetravalency of carbon, and in consequence the total number of hydrogen atoms in these compounds (hydrocarbons) is always even, *i. e.*, divisible by two, and, if any of the hydrogen atoms are replaced by other elements, the sum of the atoms with odd valencies (Cl, P, N, As) and of the remaining hydrogen atoms should always give an even number.

PHYSICAL PROPERTIES OF ORGANIC SUBSTANCES IN RELATION TO COMPOSITION AND CHEMICAL CONSTITUTION

In many cases, certain physical properties are either common to whole groups of homologous or isomeric substances, or else vary gradually with change of chemical composition. Thus the physical properties often contribute to the establishment of the true chemical constitutions of organic substances.

CRYSTALLINE FORM. The crystalline form of an organic compound is of considerable importance, since it often serves to distinguish clearly and accurately between two compounds. Two isomeric substances have often different crystalline forms.

There are, however, numerous cases of *dimorphism* or *polymorphism* (*see* Vol. I.), one of the forms always being more stable than the others.

We have already considered the relations existing between the crystalline form and chemical constitution in those stereoisomerides differing only by the *enantiomorphism* of their crystals.

P. Groth has discovered also the law of *morphotropy*, according to which a regular change is produced in the crystalline form of compounds by gradual substitution with new atoms or groups.

The relations between the crystalline forms and the chemical constitutions of substances have as yet, however, been little studied.

SOLUBILITY. The hydrocarbons and their substitution derivatives are but slightly or not at all soluble in water, but are almost all soluble in ether and in alcohol. Of the alcohols, the acids, and the aldehydes, the first terms of every homologous series are soluble in water, the solubility gradually decreasing as the number of carbon atoms in the molecule increases; these compounds are, however, relatively readily soluble in alcohol or ether. The polyhydric alcohols (glycerol, mannitol, etc.), are, however, soluble in water, but not in ether.

The compounds of the aromatic series are, in general, rather less soluble in alcohol and in water than the corresponding compounds of the fatty series.

In contact with two solvents which do not mix (*see* Vol. I., p. 93), a substance dissolves in them both in a constant ratio, independent of the relative volumes of the two solvents, but depending on the concentration and on the temperature; thus, in separating by means of ether a compound dissolved in water, a better and more rapid result is obtained by shaking many times with a little ether each time than by using fewer, but larger, quantities of ether.

Of two isomerides, that with the lower melting-point is the more soluble.

SPECIFIC GRAVITY. Isomeric compounds have different specific gravities, but with the normal hydrocarbons (C_nH_{2n+2}) the values approach one another as the number of carbon atoms increases: at about $C_{16}H_{34}$ and for higher terms the specific gravity becomes about 0·78. The specific gravity of the monobasic fatty acids is greater than 1 for the first terms of the series, but it diminishes with augmentation of the number of carbon atoms in the molecule.

MOLECULAR VOLUME. It was thought for many years that certain important rules could be deduced from the *molecular volumes* of organic compounds, that is, from the quotients, M/P, obtained by dividing the molecular weights (M) by the specific gravities (P).

In 1842 Kopp had found that, for liquids at the boiling-point, the molecular volume is very approximately equal to the sum of the atomic volumes of the component elements. For homologous compounds, the molecular volume increases by about 22 for every added CH_2 group. More recent studies (Lossen, R. Schiff, Horstmann, Traube, etc.) show, however, that these regularities are only relative and that isomeric compounds do not possess equal molecular volumes. In unsaturated series every double linking increases the molecular volume and, with closed-chain compounds, the molecular volume is less than those of the corresponding open-chain compounds with double linkings. Thus, in general, the molecular volume depends not only on *additive* factors (*e. g.*, the sum of the atomic volumes), but also on *constitutive* factors (different linkings between the carbon atoms).

MELTING-POINT. Of two isomerides, that with the more symmetrical structure has the higher melting-point. The members of a series have varying melting-points, those with odd numbers of carbon atoms having lower melting-points than those immediately below them with even numbers. There are, in addition, other less important rules, but all present exceptions. A mixture of two substances, in suitable proportions, often has a melting-point lower than that of either of the components.

BOILING-POINT. In compounds of the same series, the boiling-point rises with increase of molecular weight, the amount of the increase being about 20° per CH_2 in the methyl alcohol or formic acid series, and about 30° for benzene derivatives with methyl groups in the nucleus. The boiling-points of isologous hydrocarbons, that is, those of the same number of carbon atoms but of different series (derivatives of methane, ethylene, and acetylene), are very close to one another.

Of the isomeric compounds of the aliphatic series, the normal one boils at the highest temperature and the boiling-point is increasingly lowered by increase in the branchings.

The substitution of hydrogen by halogens and by hydroxyl groups raises the boiling-point. The ethers boil at lower temperatures than the corresponding isomeric alcohols.

HEAT OF COMBUSTION AND HEAT OF FORMATION FROM THE ELEMENTS (*see* Vol. I., pp. 60, 111, 460). The Hess-Berthelot law states that *the difference between the heats of combustion of two equivalent chemical systems is equal to the heat developed in the* *transformation of one system into the other,* that is, is equal to the *heat of formation of the latter from the elements.* In general, then, we can calculate the *heat of formation from its elements* of an organic compound by subtracting its heat of combustion from the sum of the heats of combustion of the elements composing it. As an example: the heat of combustion of methane, CH_4, at constant volume is 211,900 cals.; the heat of combustion of carbon ($C + O_2 = CO_2$) being 97,000 cals. and that of hydrogen ($H_2 + O = H_2O$) 68,400 cals., the complete combustion of methane is given by the following equation: $CH_4 + 2O_2 = CO_2 + 2H_2O = 97{,}000 + (2 \times 68{,}400) = 233{,}800$ cals., the sum of the heats of combustion of the component elements of methane. The heat of formation of methane will then be given by: $233{,}800 - 211{,}900 = 21{,}900$ cals., which also represents the heat necessary to resolve methane into its elements in order to initiate its combustion. The heat of combustion of ethyl alcohol being 340,000 cals., that of acetic acid 210,000, and that of ethyl acetate 554,000, the heat of formation of the last-named from the first two will be: $340{,}000 + 210{,}000 - 554{,}000 = - 4000$ cals.

In the analogous paraffin and olefine series, a difference of CH_2 corresponds with a variation of 150,000 to 160,000 cals. in the molecular heat of combustion.

The heats of combustion of isomeric compounds are equal, if the compounds are chemically similar, for example, methyl acetate ($CH_3 \cdot CO_2CH_3$) and ethyl formate ($H \cdot CO_2C_2H_5$), but different if the compounds are of different molecular character (for example, allyl alcohol, $CH_2 : CH \cdot CH_2 \cdot OH$, and acetone, $CH_3 \cdot CO \cdot CH_3$), compounds with multiple linking in the fatty series having higher heats of combustion than the corresponding cyclic isomerides.

These calculations are also of importance for the evaluation of the energy produced in organisms by the transformations of various foods (*see also later* in the section on Explosives).[1]

HEAT OF NEUTRALISATION. With the *organic acids* this is the same for all, namely, 13,700 cals. (*see* Vol. I., p. 99), as long as the resulting salts are not decomposed by water; with the *phenols* (cyclic compounds containing OH) the heat of neutralisation is about one-half the above value, or more if the acid character is intensified by the presence of the NO_2 group; with the alcohols it is almost zero.

OPTICAL PROPERTIES. **(1) Colour.** Most organic compounds are colourless, but if they contain iodine or the nitro-group or doubly linked nitrogen atoms ($-N = N-$), or two oxygen atoms directly united, they are generally coloured, especially in the aromatic series.

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[1] The following are the *heats of formation from the elements* of certain organic compounds, expressed in large calories per gram-molecule:

	Cals.
Naphthalene, $C_{10}H_8$: solid	− 42
Nitronaphthalene, $C_{10}H_7NO_2$: solid	− 14·7
Dinitronaphthalene, $C_{10}H_6(NO_2)_2$: solid	− 5·7
Trinitronaphthalene, $C_{10}H_5(NO_2)_3$: solid	− 3·3
Acetylene, C_2H_2 : gas	− 61·4
Ethylene, C_2H_4 : gas	− 15·4
Benzene, C_6H_6 : gas	− 10·2
Nitrobenzene, $C_6H_5NO_2$: liquid	4·2
Dinitrobenzene, $C_6H_4(NO_2)_2$: solid	12·7
Mannitol, $C_6H_{14}O_6$: solid	320
Nitromannitol, $C_6H_8N_6O_{18}$: solid	179·1
Mercury fulminate, $C_2N_2O_2Hg$: solid	− 62·9
Anthracene, $C_{14}H_{10}$: solid	− 42·4

	Cals.
Methyl alcohol, CH_3OH : liquid	62
Ethyl alcohol, C_2H_5OH : liquid	70·5
Phenol, C_6H_5OH : liquid	34·5
Trinitrophenol (picric acid), $C_6H_2OH(NO_2)_3$: solid	49·1
Sodium picrate, $C_6H_2ONa(NO_2)_3$: solid	117·5
Ammonium picrate, solid	80·1
Ether, $(C_2H_5)_2O$ gas	65·3
Ether, $(C_2H_5)_2O$ liquid	72
Glycerol, $C_3H_5(OH)_3$: liquid	165·5
Trinitroglycerol, $C_3H_5(ONO_2)_3$: liquid	196
Cellulose (cotton), $C_6H_{10}O_5$: solid	227
Nitrocellulose, solid	624–696–706

The *heats of combustion* of various organic compounds are as follow: ethyl alcohol, 340 Cals.; methyl alcohol, 182·2; mannitol, 727; cellulose, 680; terephthalic acid, 771; diphenyl, 1494; cane sugar, 1355; acetic acid, 210; benzoic acid, 772; ethyl acetate, 554; urea, 152; benzene, 779·8; dihydrobenzene, 848; tetrahydrobenzene, 892; toluene, 933; hexane, 991·2; methane, 211·9; ethane, 370·4; propane, 529·2; trimethylmethane, 687·2; ethylene, 333·4; propylene, 492·7; trimethylene, 499·4; isobutylene, 650·6; methyl chloride, 164·7; ethyl chloride, 321·9; propyl chloride, 480·2; chloroform, 70·5; dinitrobenzene (*o*-, *m*-, and *p*-), about 700; trinitrobenzene, 666 to 681; succinic acid, 357; azelaic acid, 1141; erucic acid, 3297; tribrassidinic acid, 10,236; glucose, 674; oxalic acid, 60·2; formic acid, 62·8; hydrocyanic acid, 152·3; naphthalene, 1233·6; phenol, 732; pyrogallol, 639.

In the section on Dyes are given detailed illustrations of the remarkable relations between the chemical constitution of organic compounds and their colour.

(2) **Refraction.** This is the deviation produced in the direction of a ray of light (homogeneous; for example, sodium light) on passing through a transparent liquid, and varies with the substance. The *index of refraction n* varies with the temperature, and hence with the specific gravity (d) of the substance. The relation between these two values which gives the *refraction constant R* (or *specific refractivity*) is: $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}=R$, which is almost independent of the temperature. By multiplying by the molecular weight P, the *molecular refraction* is obtained: $M=\frac{n^2-1}{n^2+2}\cdot\frac{P}{d}$, this being constant for true isomerides and changing by a constant amount for a constant change in the composition.

The molecular refraction of a compound is approximately equal to the sum of the elementary atomic refractions, but here double and triple linkings have an influence, so that these can be detected in an organic compound by means of the refraction (true double linkings of the aliphatic series are often distinguished in this way from the cyclic linkings of benzene).

(3) **Polarised Light.** Owing to the importance of this phenomenon for whole groups of organic substances, it will be useful to recall briefly in a note[1] the fundamental ideas on polarised light.

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[1] The luminous waves of white light are propagated in the cosmic ether with a velocity of about 300,000 kilometres per second, and there are physical instruments which admit of the measurement of the time required for a ray of light to traverse a few metres; indeed, Foucault measured the time taken by light to pass over a distance of 120 metres.

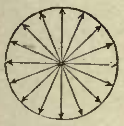

Fig. 40.

By studying the phenomena of interference of light rays, it can be shown that the vibrations of the ether in them are not longitudinal, *i. e.*, along the direction of propagation of the ray, but that the ether particles vibrate in all directions in a plane perpendicular to the direction of the ray (a transverse section of a ray is shown in Fig. 40), whilst the propagation of sound is effected by means of longitudinal vibrations in the direction of the path traversed by the sound.

A ray that enters a liquid or a non-crystalline solid, or a crystal of the regular system (cube or octahedron) gives only one refracted ray; when it enters a crystal of the rhombohedral system, *two* refracted rays are formed, one *extraordinary* and the other *ordinary*; when a ray enters a crystal of any other system, *two* refracted rays are formed, but these rays both behave like the *extraordinary* ray, and, like the latter, they do not obey the laws of refraction, according to which an incident ray, perpendicular to a medium with parallel faces, should not be deviated or refracted.

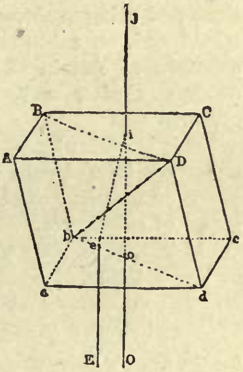

Fig. 41.

If a ray of light, *J i* (Fig. 41), strikes a rhombohedral crystal of Iceland spar perpendicularly to the face *A B C D*, the ray divides into two. The one, *i o O*, continues in the same direction, the other, *i e*, is deviated, but when it emerges from the crystal assumes the direction *e E*, parallel to the original direction. The two parallel rays leaving the crystal have equal luminosities, but *o O* follows the ordinary laws of refraction (*vide supra*) and is called the *ordinary ray*, whilst the other, *e E*, does not obey these laws and is termed the *extraordinary ray*.

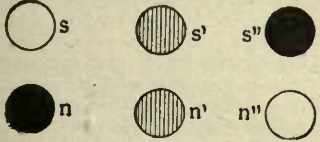

Fig. 42.

If the crystal is rotated about the incident ray *J i* as an imaginary axis, the position of the ray *o O* does not change, whilst the ray *e E* moves in the sense in which the crystal is rotated. The extraordinary ray *i e* always lies in the plane of the *principal axis* of the crystal *d b B D*, which passes through the principal axis of the crystal *b O* and is parallel to it. These two rays emerging from the crystal have, however, properties different from those of the incident ray *J i*; in fact, if either of the two refracted rays (*e E* or *o O*) is passed into a second rhombohedron of Iceland spar, two new rays (*double refraction*) are obtained, but the intensities of the two rays vary according to the relative positions of the two crystals. Thus, if a ray emerging from the first crystal passes perpendicularly into the second crystal, the principal section of which is parallel to that of the first, no double refraction is observed, only one ray leaving the second crystal (*s* in Fig. 42, the second hypothetical ray *n* being not visible and marked black in the figure). If, however, the second crystal is rotated round the imaginary axis, *o O*, a second ray

Those organic substances are called *optically active* which rotate the plane of polarised light. Some substances are optically active in the crystalline state (not in the amorphous state or in solution), and hence the action on polarised light is due in these cases to the peculiar arrangement of the molecules; very few are active in both the crystalline and amorphous states, the majority exhibiting activity only in a dissolved condition (sugars, etc.), where the phenomenon depends on the arrangement of the atoms or groups of atoms in the molecule. This holds also for camphor and oil of turpentine, which are active even in the form of vapour.

The longer the layer (l) and the greater the concentration of the solution (p = grams of dissolved substance in 100 of solution) traversed by the polarised light, the greater will be the rotation of the plane of polarisation. Referring the observed rotation α to a length of 10 cm. of a solution containing 1 gram of pure substance in 1 c.c. ($= pd/100$, where d is the specific gravity of the solution), we get the *specific rotatory power* of the solution for the yellow sodium light (D line of the spectrum [1]) by means of the following formula: $[\alpha]_D = \frac{100\,\alpha}{l.d.p}$. For active liquid substances examined without solvent, $[\alpha]_D = \frac{\alpha}{l.d}$. The *molecular rotation* (for a molecular weight M) is given by: $(M) = \frac{M \cdot [\alpha]}{100}$.

For a definite solvent and given concentration and temperature, every active substance (and such are almost all those containing *asymmetric carbon*, *see* p. 19) has a constant and characteristic specific rotatory power, either to the right (+) or to the left (—). This varies with the nature and degree of electrolytic dissociation of the solvent, and increases with dilution and diminishes with rise of temperature; for purposes of comparison, it is usually determined at 20°, and is then indicated thus: $[\alpha]_D^{20}$. By repeating the determinations and using moderately high concentrations, the influence due to the solvent is determined and, on subtracting this, the *true specific rotation* is obtained. Freshly prepared solutions of certain sugars exhibit the phenomenon of *muta-rotation*, which, however, disappears after a time or on boiling the liquid, the normal rotation then being given.

This important property of optically active compounds is studied by means of special apparatus termed *polarimeters*, which are used particularly in the analysis of sugars (and hence often called *saccharimeters*), and will be described in the section dealing with this group of substances.

MAGNETIC ROTATORY POWER. All liquids in a magnetic field produce a greater or less rotation of the plane of polarised light, according to their chemical composition and in conformity with the laws governing the refractivity of light. In many cases the

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(extraordinary) suddenly appears, *i. e.*, double refraction takes place, and whilst the luminosity of the new ray increases, that of the first ray becomes weaker and when the principal sections of the two crystals form an angle of 45°, the two rays have equal intensities (s', n'); if the crystal is rotated still more, the extraordinary ray becomes more luminous, whilst the first (*ordinary*) decreases in luminosity, and when the principal sections are perpendicular to one another, the intensity of the ordinary ray (s') is zero (*i. e.*, it is not seen), only the extraordinary ray being seen with its maximum intensity (n''). The light rays emerging from the second rhombohedron are hence different from those emerging from the first, the latter not varying in intensity when the prism is rotated, whilst the others do so.

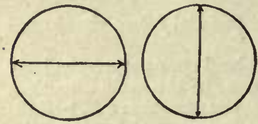


FIG. 43.

The rays leaving the first prism are called *polarised*, and are distinguished from ordinary light rays, since, on passing through a second prism, they undergo the changes described above. A polarised ray passes as an *ordinary ray* through a second rhombohedron only when its *plane of polarisation* is parallel to the principal section of the new rhombohedron. It is found, then, that the plane of polarisation of the polarised ordinary ray is perpendicular to the plane of polarisation of the extraordinary ray. Hence, the rays E and O vibrate in planes perpendicular to one another (Fig. 43).

POLARISATION BY REFLECTION. Polarised light rays are obtainable, not only by double refraction, but also *by reflection* under special conditions, namely, when a light ray falls on a plate of glass at an incident angle of 54° 35′.

Polarised light is also obtained by simple refraction, by passing a ray of light through a series of superposed parallel plates or through sheets of tourmaline.

[1] The angle of rotation varies with the length of the light-wave and is greater for violet rays (which have a smaller wave-length and are hence refracted more) and less for red rays (which have a greater wave-length and are hence less refrangible).

constitution of a substance has been determined or confirmed by measuring the *molecular magnetic rotation.*

ELECTRICAL CONDUCTIVITY. We must refer the reader to the detailed treatment of electrolytic dissociation and the theory of ions in Vol. I. (pp. 94 *et seq.*), as the same is directly applicable to organic compounds, especially as regards the conductivity of salts, acids, bases, etc.

CLASSIFICATION OF ORGANIC SUBSTANCES

These are usually divided into two large series :

(1) That of the *open-chain* carbon compounds or *methane derivatives*, termed also compounds of the *fatty* or *aliphatic series*, as all the fats and many of their derivatives belong here. This series embraces two groups of substances: that of the *saturated compounds* or *derivatives of the paraffins* (C_nH_{2n+2}) and that of the *unsaturated compounds* (*olefines*, C_nH_{2n} and derivatives of *acetylene*, C_nH_{2n-2}).

(2) That of the *closed-chain* carbon derivatives, these being subdivided into :

(*a*) The *isocyclic* or *carbocyclic compounds*, which have the closed chain formed either of nuclei of six carbon atoms with six available valencies to every nucleus (C_nH_{2n-6}, *benzene derivatives* or *aromatic compounds*) or of nuclei with different numbers of carbon atoms, but more highly hydrogenated (*cycloparaffins*, *cyclo-olefines*, and *polymethylene derivatives*).

(*b*) The *heterocyclic compounds*, the closed chain of which contains atoms (N, P, S, O, etc.) other than carbon.

The hydrogenated compounds of carbon are called *hydrocarbons* and are termed *saturated* when the carbon atoms are joined by single valencies, and the other valencies are all satisfied by hydrogen. These saturated hydrocarbons cannot combine with a further quantity of hydrogen.

Hydrocarbons containing carbon atoms united by double or triple linkings are called *unsaturated hydrocarbons*, and these can combine with further quantities of hydrogen, thus becoming saturated. Other important hydrocarbons are those with closed chains, which we shall study in Part III of this book.

Usually in homologous series, with increase in the number of carbon atoms, the compounds pass from the gaseous to the liquid and solid states; *e. g.*, formic acid, with one carbon atom, is a liquid and boils at 99°, while the homologous acid with sixteen carbon atoms is a solid and boils at over 300°.

OFFICIAL NOMENCLATURE

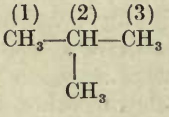
With the continuous development of organic chemistry and the multiplication of new compounds, the need was often felt for a rational method of naming compounds which would facilitate the treatment of these vast numbers of compounds. For the new nomenclature to be the more efficacious it needed to be international, because everywhere there reigned the greatest confusion in the naming of chemical compounds, this referring either to the starting substance or to the new group to which they belonged, or to the use for which they were intended, or to the molecular constitution, and so on, so that the same substances often had four or five names.

In 1892, at an International Convention of Chemists at Geneva, a general system of nomenclature of organic compounds was agreed on. This is gradually being introduced into chemical literature, and, although not always felicitous, it has helped to simplify the naming of compounds and to reduce the confusion.

Following only in part the ideas proposed by Kolbe many years before, the new nomenclature derives the names of all compounds from the names of the fundamental hydrocarbons to which the compounds can be referred, taking into account the number of carbon atoms present as well as the nature of the linking. Thus, to the fundamental names of the saturated hydrocarbons: methane, ethane, propane, butane, pentane, hexane, heptane, etc., the addition of the suffix *ol* indicates the presence of the hydroxyl group —OH, and thus an alcohol, for example, *methanol* (methyl alcohol), *ethanol* (ethyl alcohol), etc.; the suffix *al* serves to denote the *aldehyde* group $\left(-\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \diagdown\mathrm{H}\end{array}\right)$, thus, *e. g.*, *methanal* = formaldehyde, *ethanal* = acetaldehyde, etc.; the suffix *one* indicates the *ketonic* group (—CO—), thus, *propanone* (commonly called acetone), etc. The suffix *oic* is used to indicate the organic *acids*, which all contain the characteristic *carboxyl* group $\left(-\mathrm{CO_2H},\ i.\ e.,\ -\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \diagdown\mathrm{HO}\end{array}\right)$, and thus we have *methanoic* (formic) acid, *ethanoic* (acetic) acid, *propanoic* (propionic) acid, *butanoic* acid, *pentanoic* acid, etc.

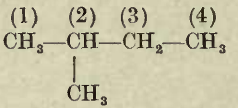
For the unsaturated doubly linked hydrocarbons the fundamental hydrocarbon ethylene is distinguished with the name of *ethene*, and that with a triple bond between the two carbon atoms (acetylene) is called *ethine.*

With the saturated hydrocarbons, isomerides with branched chains are referred to the *normal hydrocarbon* (*i. e.*, non-branched) with the longest chain present in the molecule, numbering progressively its carbon atoms, starting at the end nearest to the point where branching occurs. The name begins with that of the residue of the side-chain,[1] then follow the successive numbers of the atoms of the normal chain where side-chains join on, and finally comes the name of the normal hydrocarbon.



$$\begin{array}{ccccc}(1)&&(2)&&(3)\\ \mathrm{CH_3}&-&\mathrm{CH}&-&\mathrm{CH_3}\\ &&|&&\\ &&\mathrm{CH_3}&&\end{array}$$

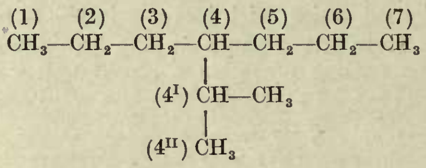
bears the official name *methyl-2-propane* (some call it *propyl-2-methane*), and isopentane,



$$\begin{array}{ccccccc}(1)&&(2)&&(3)&&(4)\\ \mathrm{CH_3}&-&\mathrm{CH}&-&\mathrm{CH_2}&-&\mathrm{CH_3}\\ &&|&&&&\\ &&\mathrm{CH_3}&&&&\end{array}$$

that of *methyl-2-butane*, etc.

When there are also secondary ramifications a supplementary numbering is used; thus, for isodecane,



$$\begin{array}{ccccccccccccc}(1)&&(2)&&(3)&&(4)&&(5)&&(6)&&(7)\\ \mathrm{CH_3}&-&\mathrm{CH_2}&-&\mathrm{CH_2}&-&\mathrm{CH}&-&\mathrm{CH_2}&-&\mathrm{CH_2}&-&\mathrm{CH_3}\\ &&&&&&|&&&&&&\\ &&&&(4^{\mathrm{I}})&&\mathrm{CH}&-&\mathrm{CH_3}&&&&\\ &&&&&&|&&&&&&\\ &&&&(4^{\mathrm{II}})&&\mathrm{CH_3}&&&&&&\end{array}$$

the official name would be metho-4^{I}-ethyl-4-heptane.

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[1] The names of the *hydrocarbon residues*, called also *alkyl* groups, are formed from the root of the name of the corresponding hydrocarbon, with the suffix *yl*; thus, with methane corresponds the *methyl* residue, $-\mathrm{CH_3}$; with ethane, *ethyl*, $-\mathrm{C_2H_5}$; and then follow *propyl*, $-\mathrm{C_3H_7}$; *butyl*, $-\mathrm{C_4H_9}$, etc.

PART II. DERIVATIVES OF METHANE

AA. HYDROCARBONS

THE hydrocarbons form a very large and important group of organic substances, which are composed only of hydrogen and carbon, and give rise to other most varied substances by replacement of part or all of the hydrogen by other elements or groups.

For the reasons given on p. 29, they are divided into two main groups: saturated and unsaturated hydrocarbons.

(a) SATURATED HYDROCARBONS

These are called saturated because the linkings between the carbon atoms are simple ones and all the valencies are saturated, so that hydrogen, chlorine, bromine, iodine, ozone, etc., cannot be *added* to them; the halogens do, indeed, react with saturated hydrocarbons (fluorine reacts with methane even at − 187°), but by *substitution* of the hydrogen atoms.

They are called also *paraffins*, since, like the common solid paraffin waxes, all the saturated hydrocarbons resist, in the *cold*, the action of chromic acid, potassium permanganate, and concentrated nitric and sulphuric acids, and are, in general, compounds with an almost indifferent chemical character. In the hot, however, energetic oxidising agents convert them, more or less completely, into carbon dioxide and water.

As a general rule, these hydrocarbons are insoluble in water and only some of them dissolve in alcohol, whilst almost all are soluble in ether.

Of the *direct* or *continuous* (*normal*) and *branched* (isomeric) *open chains*, mention has already been made on pp. 17 and 29, and it may be seen how, starting from the hydrocarbon, C_4H_{10}, the number of isomerides rapidly increases: 2 for butane; 3 for pentane, C_5H_{12}; 5 for hexane, C_6H_{14} (all known); while for $C_{12}H_{26}$ the number theoretically possible is 355 and for $C_{13}H_{28}$, 892, only some of which are, however, known. All the terms of the *paraffin series* can be represented by the general formula C_nH_{2n+2}, and the following Table (p. 32) gives the name, formula, boiling-point, and melting-point of the principal known paraffins. The official nomenclature is described on p. 29.

The first members of the series are gases, then follow liquids as far as C_{15}, and beyond that, solids, the boiling- and melting-points rising with increase of the molecular weight (*see* p. 25).

NATURAL FORMATION AND GENERAL METHODS OF PRODUCTION. These hydrocarbons, from the lowest gaseous members to the highest solid ones (paraffin wax), occur abundantly as the almost exclusive components of petroleum (especially that from America), and it is not difficult to separate single individuals from these complex mixtures.

In many natural emanations of inflammable gas, methane and, to some extent, ethane are found in large proportions, and the solid hydrocarbons occur also in *ozokerite* (*which see*).

The gaseous, liquid, and solid hydrocarbons are formed abundantly on the dry distillation of wood, lignite, bituminous schists, and coal, especially *boghead* and *cannel coals*, which are relatively rich in hydrogen (*see* Illuminating Gas);

SATURATED HYDROCARBONS, C_nH_{2n+2}

(After hexane, only the *normal* ones are given)

			Melting-point.	Boiling-point.		Specific Gravity.	
CH_4	Methane		−184°	−164° (760 mm.)		0·415 (−164°) 0·555 (0°, 760 mm.)	
C_2H_6	Ethane		−172·1°	−84·1° (749 mm.) (0° at 23·8 atm.)		0·446 (0°)	
C_3H_8	Propane		− 45°	−44·5° (0· at 5 atms.)		0·535 (0°, liquid)	
C_4H_{10}	Butanes	normal	—	+ 1°		0·600 (0°)	
		iso	—	−17°		0·6029 (0°)	
C_5H_{12}	Pentanes	normal	− 200°	+36·3°		0·454 (0°)	
		iso	—	+30·4°		0·622	at 20°
		tertiary	− 20°	+ 9°		—	
C_6H_{14}	Hexanes	normal	—	69°		0·6603	
		dimethylisopropylmethane	—	58°		0·666	
		dimethylpropylmethane	—	62°		0·6766 (0°)	
		methyldiethylmethane	—	64°		0·677	at 20°
		trimethylethylmethane	—	49·6°		0·6488	
C_7H_{16}	Heptane		—	98·3°		0·683	
C_8H_{18}	Octane		—	125·8°		0·702	
C_9H_{20}	Nonane		− 51°	150°		0·718	
$C_{10}H_{22}$	Decane		− 31°	173°		0·7467	
$C_{11}H_{24}$	Undecane		− 26°	196°		0·7581	at the melting-point
$C_{12}H_{26}$	Dodecane		− 12°	215°		0·7684	
$C_{13}H_{28}$	Tridecane		− 6°	234°		0·775	
$C_{14}H_{30}$	Tetradecane		+ 4°	252°		0·775	
$C_{15}H_{32}$	Pentadecane		+ 10°	270°		0·776	
$C_{16}H_{34}$	Hexadecane		18°	287°		0·775	
$C_{17}H_{36}$	Heptadecane		22°	303°		0·777	
$C_{18}H_{38}$	Octodecane		28°	317°		0·777	
$C_{19}H_{40}$	Nonodecane		32°	330°		0·777	
$C_{20}H_{42}$	Eicosane		37°	205°	at 15 mm. pressure	0·778	
$C_{21}H_{44}$	Heneicosane		40°	215°		0·778	
$C_{22}H_{46}$	Docosane		44°	224°		0·778	
$C_{23}H_{48}$	Tricosane		48°	234°		0·779	
$C_{24}H_{50}$	Tetracosane		51°	243°		0·779	
$C_{25}H_{52}$	Pentacosane		53·5°	—		—	
$C_{26}H_{54}$	Hexacosane		58°	—		—	
$C_{27}H_{56}$	Heptacosane		60°	270°		0·780	
$C_{28}H_{58}$	Octocosane		60°	—		—	
$C_{29}H_{60}$	Nonocosane		63°	about 340°		—	
$C_{31}H_{64}$	Hentriacontane		68°	302°		0·781	
$C_{32}H_{66}$	Dotricontane (Dicetyl)		70°	310°		0·781	
$C_{35}H_{72}$	Pentatricontane		75°	331°		0·782	
$C_{60}H_{122}$	Hexacontane		101°	—		—	

also when petroleum residues are strongly heated under pressure (*cracking*), hydrocarbons similar to petroleum and also gaseous ones are formed.

Of the numerous synthetical methods of preparation of the saturated hydrocarbons, the following more important ones may be mentioned:

(*a*) Any member of the series may be obtained by reducing the halogen derivatives of the hydrocarbon (obtained from the alcohols and the halogen hydracids) by means of *nascent hydrogen* (generated by sodium amalgam, or by a solution of sodium in absolute alcohol, or by zinc and hydrochloric acid, or by heating zinc and water at 160°) or of hydriodic acid, especially in the presence of red phosphorus (which transforms the iodine into hydriodic acid): $C_2H_5I + H_2 = HI + C_2H_6$; $C_2H_5I + HI = I_2 + C_2H_6$ (*see* Table of the halogen derivatives of the hydrocarbons).

(*b*) The alcohols give paraffins when heated with hydriodic acid:

$$C_2H_5 . OH + 2HI = H_2O + I_2 + C_2H_6.$$

(*c*) By the interaction of zinc alkyls and water:

$$Zn(C_2H_5)_2 + 2H_2O = Zn(OH)_2 + 2C_2H_6.$$

(*d*) From unsaturated hydrocarbons by the action of hydrogen, *e. g.*, by heating acetylene and hydrogen at 400° to 500°, or in presence of platinum-black.

(*e*) By eliminating a molecule of carbon dioxide from the organic acids and salts by heating with soda-lime or sodium alkoxide:

$$CH_3 . COONa \text{ (sodium acetate)} + NaOH = Na_2CO_3 + CH_4.$$

(*f*) By the action of sodium or of zinc on the zinc alkyls or alkyl iodides in ethereal solution in a closed tube (Wurtz), two alkyl groups, even different ones, being condensed:

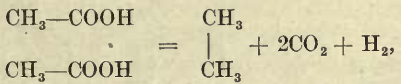
(1) $2CH_3I + Na_2 = 2NaI + C_2H_6.$
(2) $C_2H_5I + C_4H_9I + Na_2 = 2NaI + C_2H_5 . C_4H_9.$
(3) $2CH_3I + Zn(CH_3)_2 = ZnI_2 + 2C_2H_6.$

(*g*) During the last few years it has been shown that magnesium is much more active than zinc in many organic syntheses (*see later*, Grignard Reaction), and with alkyl iodides dissolved in absolute ether, magnesium forms magnesium alkyl salts which, in decomposition by means of water or dilute acid or ammonia with solid ammonium chloride, yield the saturated hydrocarbons: $C_2H_5I + Mg = C_2H_5MgI$, and this $+ H_2O = C_2H_6 + Mg(OH)I$. In part, however, the magnesium fixes the halogen, and then two alkyl residues condense, forming a hydrocarbon of double the number of carbon atoms:

$$2C_2H_5I + Mg = MgI_2 + C_4H_{10}.$$

(*h*) Sabatier and Senderens' catalytic process, for which *see* p. 35.

(*i*) By electrolysing acetic acid:



$$\begin{matrix} CH_3\text{—}COOH \\ \\ CH_3\text{—}COOH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2 + H_2,$$

the hydrogen going to the negative pole and the hydrocarbon and carbon dioxide to the positive one.

METHANE (MARSH GAS), CH_4

This is a gas which is often found ready formed in nature, and in former times it was always confused with hydrogen (inflammable air). Pliny refers to the gases which exude from the earth in certain regions and are inflammable (these are probably the *sacred fires* of the ancient Chaldeans). Basil Valentine (1500) records fires in mines preceded by the emanation of asphyxiating, poisonous vapours, which are dispersed and rendered innocuous by the fire issuing from the rock. Also Libavius (1600) speaks of the inflammable and explosive gas of mines, and in 1700–1750 history records numerous explosions, especially in coal-mines. In was Volta who, in 1776, when studying the same gas, which is also evolved in marshes, showed that it differs from hydrogen, since in burning it requires double its volume of oxygen and forms carbon dioxide. In 1785 Berthollet proved that the gas is formed of carbon and hydrogen, and later Henry, Davy, and Berzelius determined its true composition.

It occurs abundantly as exhalations from the earth near the Caspian Sea (sacred fires of Baku) and in the peninsula of Apsheron is used for heating purposes.

At Pittsburg there are great wells of pure methane, and it is found also near Glasgow, in the Crimea, and also in Italy, at Pietra Mala (Bologna), in Ferrarese, in Piacenza (Salsomaggiore), etc. It always occurs in coal-mines, being formed from the coal by slow decomposition and remaining occluded in the coal under great pressure, together with carbon dioxide and nitrogen (*see below :* Industrial Uses).

It is invariably developed in marshy places where there is organic matter putrefying under water. It is found in the gas of the intestines of man and, still more, of the ruminants (about 50 per cent. CH_4), being produced by the action of enzymes on the cellulose ($C_6H_{10}O_5$) of vegetable matter : $C_6H_{10}O_5 + H_2O = 3CO_2 + 3CH_4$.[1] Illuminating gas contains up to 40 per cent. of it.

PROPERTIES. It was one of the *permanent gases* (Vol. I., p. 29); it liquefies at — 164° and solidifies at — 186°. It has the sp. gr. 0·559 and 1 litre weighs 0·720 gram. It has no colour or taste, but a faint garlicky odour. It dissolves slowly but appreciably in fuming sulphuric acid, but only very slightly in water (0·05 per cent.). It is readily inflammable and burns with a faintly luminous flame; mixed with oxygen (heat of combustion, 9433 cals. per cu. metre; *see also* p. 26) it forms a *detonating mixture* (inflammable at 667°, whilst the mixture with ethane inflames at 616° and that with propane at 547°), the maximum effect being obtained with 1 vol. of methane and 2 vols. of oxygen ($CH_4 + 2O_2 = CO_2 + 2H_2O$).[2] Mixed with air, it forms the *fire-damp* of coal-mines, which is very dangerous owing to its explosibility,[3] although

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[1] The percentage composition of *intestinal gas* varies with the nature of the food taken.

	Flesh	*Mixed*	*Milk*	*Vegetable*
H . . .	35·5	25·8	54·2	1·5
CH_3 . . .	—	15·5	—	49·3

[2] Explosive gas mixtures (Teclu, 1907):

	Maximum effect.	Minimum effect.	
		With excess.	With deficit.
	Vols.	Vols.	Vols.
100 volumes of air + hydrogen . .	40	170	8–10
,, ,, ,, + methane . . .	10	—	3·6
,, ,, ,, + coal gas . . .	17–20	31	4·7
,, ,, ,, + acetylene . .	8·3	130	2·4
,, ,, ,, + ether vapour . .	3·3	8	1·5
,, ,, ,, + alcohol vapour .	6·5	—	3·4

[3] Since the methane is occluded under great pressure between the layers of coal, its development and hence also the danger is greater when the atmospheric pressure diminishes or when the temperature rises. To prevent explosions of firedamp, the miners use the Davy lamp (Vol. I. p. 464). Considerable danger of explosion more often exists in mines owing to the *coal dust* suspended in the air of the galleries and behaving like a *pyrophoric substance* (Vol. I., p. 189); as a precautionary measure, air is continually circulated through the galleries by powerful fans, and the air and the walls are moistened by means of pulverisers. Mines containing much dust are dangerous even if the Davy lamp is used, since the particles of coal passing through the gauze into the lamp may issue in a red-hot condition. Hardy has constructed an apparatus which allows of the quantity of methane being determined from the sound produced by the mixture of air and methane in traversing an organ pipe.

In 1913 Haber and Leiser improved the apparatus into the *firedamp whistle*, which allows the sound produced with pure air to be compared at any instant with that given by the methane-it is not poisonous, since miners can withstand an atmosphere containing 9 per cent. of methane; if there is not more than this proportion, it produces a kind of pressure at the forehead, which ceases immediately pure air is breathed.

By an electric discharge or in a red-hot tube, it decomposes into carbon and hydrogen, and a few unsaturated hydrocarbons, with traces of benzene and naphthalene.

PREPARATION IN THE LABORATORY. Besides by the general methods given above, methane is formed by passing a mixture of carbon monoxide or dioxide with hydrogen over reduced nickel (catalyst) heated at 250° (Sabatier and Senderens): $CO + 3H_2 = H_2O + CH_4$ (*see note*, p. 58). Attempts have recently been made to put this method on an industrial basis, by transforming the carbon monoxide and dioxide of water-gas into methane (Ger. Pat. 183,412). Pure methane is formed by passing a mixture of carbon disulphide vapour and hydrogen sulphide over red-hot copper (Berthelot): $CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4$; also by treating aluminium carbide with water: $C_3Al_4 + 12H_2O = 4Al(OH)_3 + 3CH_4$.

Ipatiev obtains methane by heating carbon in presence of excess of hydrogen at 520°, reduced nickel (with CO_2 and H_2 the reaction is less complete) being used as catalyst.

In the laboratory it is usually prepared from an intimate mixture of one part of crystalline sodium acetate with four parts of soda-lime (or better, with four parts of baryta or with a mixture of anhydrous sodium carbonate and dry powdered calcium hydroxide). This is heated in a retort or in a hard glass tube until gas begins to be evolved, the temperature being then kept constant. As impurities, it contains a little hydrogen and acetylene, so that, before collecting the methane, the gas is passed over pumice moistened with concentrated sulphuric acid.

Chemically pure, it may be obtained, by the general method, from zinc ethyl and water.

INDUSTRIAL USES. For several centuries, the inflammable gases issuing from the earth and from petroleum have been utilised at Baku for heating lime-kilns, and nowadays are employed for various other industrial and domestic purposes. The amounts of natural gas used at Baku were 46·5 million cu. metres in 1905, 96·3 million in 1906, and 117 million in 1907, the composition being: CO_2, 3 to 3·8 per cent.; C_nH_m, 1·2 to 2·6 per cent.; O, 7 to 7·6 per cent.; CH_4, 54·8 to 60·2 per cent.; H, 13·58 to 0·8 per cent.; and N, 20·4 to 25 per cent. In North America, as far back as 1821, these natural emanations were used as illuminating gas. The most important discoveries, made at Pittsburg in 1882, resulted in 98 per cent. of the American production being obtained from this source in 1900; after 1905, the wells of Louisiana also acquired importance, and later the greatest output was obtained in the state of Kansas (to the value of £440,000 in 1905 and £1,520,000 in 1908). At St. Louis 300,000 cu. metres were consumed per day in 1910.

In 1912 the wells of Caddo, near Shreveport (Louisiana), yielded as much as 280,000 cu. metres per day of gas (95 per cent. CH_4, 2·56 per cent. N, 2·34 per cent. CO_2, 0·01 per cent. H), these wells being about 300 metres deep and the gas being furnished at a pressure of about 40 atmospheres. The gas is led in mains to Shreveport and sold at 5 cents per cu. metre for domestic purposes and at about 2 cents for industrial uses, this allowing electrical energy to be obtained more cheaply than from Niagara Falls. The utilisation of the gas at

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air mixture and is capable of detecting 0·2 to 0·5 per cent. of methane. Observation of the luminous aureole formed round the flame of a safety lamp with a slightly twisted wick is not capable of revealing differences of 2 to 3 per cent. of CH_4, so that the explosive limit (5·5 per cent. of CH_4) may be reached without discovery in this way.

When mines are being excavated, *safety explosives* (*which see*) are used to avoid fires and explosions. Sometimes the coal ignites in certain parts of the mine; in such cases, work is not suspended, but these parts are isolated by walls, and if the fire becomes threatening, recourse is had (usually with success) to the sealing of the mine and subsequent inundation with water or filling of the galleries with carbon dioxide. When an explosion occurs in a mine, a large amount of carbon monoxide is formed, which poisons the workers, who can, however, sometimes be saved if they can be made to breathe, sufficiently promptly, under a bell containing compressed air (Mosso's Method; Vol. I., p. 190).

the present day is carried out rationally and on a vast industrial scale, the gas (issuing from suitably constructed wells) passing to large gasometers which distribute it directly to factories and houses, where it is employed for power, heating, and lighting (with the Auer mantle), the price being about 3½ cents per cubic metre.

The gas utilised in the United States of America represents the following values in pounds sterling: in 1882, 40,000; in 1890, 1,400,000; in 1894, 2,800,000; in 1899, 4,000,000; in 1906, 9,600,000; in 1908, 11·4 milliards of cu. metres were used and in 1911, 15 milliards (£14,000,000). These gases have the sp. gr. 0·624 to 0·645, and a calorific value of about 9000 cals. per cu. metre. The composition varies between the following limits: CH_4, 80 to 95 per cent.; H, 0·5 to 1·5 per cent. (sometimes 15 per cent.); C_2H_4, 0·3 to 4 per cent.; CO, 0 to 0·6 per cent.; CO_2, 0·3 to 2·5 per cent.; O, 0·35 to 0·80 per cent.; N, 0·5 to 3·5, together with traces of H_2S.

In Canada, 400 wells are being used, giving, in 1907, gas of the value of £120,000. In England, wells have been sunk since 1900 which yield 400,000 cu. metres of gas per day. The spring at Wels, in Austria, which gave 57,000 cu. metres of gas per day in 1894, yielded only 500 cu. metres per day in 1901.

At Kissarmas, near Sarmas (Hungary), a well yielded in 1909 1,700,000 cu. metres of almost pure methane per twenty-four hours at a pressure of 30 atmospheres. The first source of natural gas in Germany was discovered in 1910 at Neuengamme at a depth of 248 metres, the gas issuing at 25 atmospheres' pressure and maintaining for a long time the percentage composition: CH_4, 91·6; H, 2·3; CO_2, 0·2; O, 0·7; N, 4·4; heavy hydrocarbons, 0·8. The gases obtained from the deposits of potash salts at Stassfurt (*see* Vol. I., p. 530) have a varying composition: CH_4, 5 to 40 per cent.; H, 11 to 80 per cent.; N, up to 40 per cent.; helium and neon, 1 per cent. The value of these methane springs may be estimated from the fact that one ton of coal yields only 300 cu. metres of gas.

The gas which is used at Salsomaggiore (Piacenza) for public lighting purposes and which issues from the earth together with petroleum and saline waters containing iodine, has the sp. gr. 0·692, and the following percentage composition (Nasini and Anderlini, 1900): CH_4, 68; C_2H_6, 21; heavy hydrocarbons, 1; N, 8. In Italy, 1,520,000 cu. metres of these gases, of the value £2280, were used altogether in 1902, 6,737,500 cu. metres in 1908, and 8,270,000 cu. metres, of the value £8760, in 1909.

Important sources of these gases have been recently discovered in Hungary (in 1911 at Klausenburg, where the well gave 800,000 cu. metres per day of gas containing 99 per cent. of methane in 1913), England (at Heathfield a well gave as much as 500,000 cu. metres per day), and in Denmark (since 1872).

ETHANE, C_2H_6

This gas is found dissolved in crude petroleum, and is one of the principal constituents of the North American gas-wells of Delamater, near Pittsburg.

It is a gas which can be liquefied at 0° by means of a pressure of 24 atmospheres and then has the sp. gr. 0·446; at the ordinary pressure it becomes liquid and boils at — 84° and is solid and melts at — 172°. It is almost insoluble in water; 1 vol. of absolute alcohol dissolves 1½ vols. of it. It burns with a faintly luminous flame, and is more readily soluble than methane. In the laboratory it is prepared by the general methods already given (p. 33).

PROPANE, C_3H_8 (METHYLETHYL, $CH_3 \cdot C_2H_5$ or DIMETHYLMETHANE, $CH_2(CH_3)_2$)

This is a gas like ethane and becomes liquid at — 44°, or under 5 atmospheres' pressure at 0°, the liquid at 0° having the sp. gr. 0·535; it solidifies and melts at — 45°. It is slightly soluble in water, and absolute alcohol dissolves 6 vols. of it. With water under pressure and at temperatures below 0° it forms a solid hydrate, which decomposes at + 8·5°. The illuminating power of propane is about 1½ times that of ethane. It is best prepared, in the laboratory, by reducing isopropyl iodide by means of the copper-zinc couple, or by reducing acetone or glycerol with hydriodic acid:

$$\underset{\text{glycerol}}{C_3H_5(OH)_3} + 6H = 3H_2O + C_3H_8 \quad \text{or} \quad \underset{\text{acetone}}{CH_3 \cdot CO \cdot CH_3} + 4H = H_2O + C_3H_8.$$

BUTANES, C_4H_{10} (Two Isomerides)

(*a*) *Normal Butane*, $\mathrm{CH_3\cdot CH_2\cdot CH_2\cdot CH_3}$ (*diethyl*), is a gas which liquefies at + 1°, and at 0° has the sp. gr. 0·600. It is found in Pennsylvanian petroleum, and is prepared in the laboratory by the ordinary methods (p. 33).

(*b*) *Isobutane*, $\mathrm{CH_3\cdot CH}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}}$ (*trimethylmethane* or *methylpropane*), is a gas which becomes liquid at — 115°; it is contained in petroleum and is prepared by the usual methods in the laboratory.

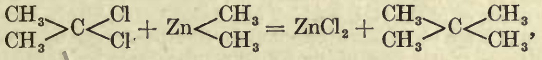
PENTANES, C_5H_{12}

These hydrocarbons are found especially in the petroleum products boiling a little above 0°, and are placed on the market under the names of *rhigolene* and *cymogen* for anæsthetic purposes and for the manufacture of artificial ice. The three isomerides predicted by theory are known:

(*a*) *Normal pentane*, $\mathrm{CH_3\cdot [CH_2]_3\cdot CH_3}$, is a colourless, mobile liquid boiling at + 37·3°, having the sp. gr. 0·454 at 0°, and solidifying only at about — 200°; it is hence used for making low-temperature thermometers, and as a lubricant in the Claude liquid air machine (Vol. I., p. 345). It occurs abundantly in Pennsylvanian petroleum.

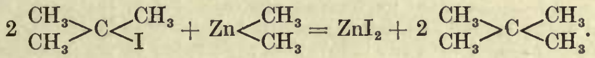
(*b*) *Isopentane*, $\mathrm{CH_3\cdot \underset{\substack{|\\ CH_3}}{CH}\cdot CH_2\cdot CH_3}$ (methyl-2-butane or ethylisopropyl), is a light colourless liquid boiling at 30·4°, and having the sp. gr. 0·622 at 20°. It is found in large quantities in petroleum, and may be prepared artificially from isoamyl iodide by the ordinary methods (p. 33).

(*c*) *Tetramethylmethane*, $\substack{\mathrm{CH_3}\\ \mathrm{CH_3}}{>}\mathrm{C}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}}$ (dimethyl-2-propane), is found in the gases from petroleum, and is liquid at + 9° and solid at — 20°. It may be obtained in the laboratory either by chlorinating acetone, $\mathrm{CH_3\cdot CO\cdot CH_3}$, by means of phosphorus pentachloride and treating the dichloropropane thus formed with zinc methyl:



$$\substack{\mathrm{CH_3}\\ \mathrm{CH_3}}{>}\mathrm{C}{<}\substack{\mathrm{Cl}\\ \mathrm{Cl}} + \mathrm{Zn}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}} = \mathrm{ZnCl_2} + \substack{\mathrm{CH_3}\\ \mathrm{CH_3}}{>}\mathrm{C}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}},$$

or from tertiary butyl iodide by the action of zinc methyl:



$$2\ \substack{\mathrm{CH_3}\\ \mathrm{CH_3}}{>}\mathrm{C}{<}\substack{\mathrm{CH_3}\\ \mathrm{I}} + \mathrm{Zn}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}} = \mathrm{ZnI_2} + 2\ \substack{\mathrm{CH_3}\\ \mathrm{CH_3}}{>}\mathrm{C}{<}\substack{\mathrm{CH_3}\\ \mathrm{CH_3}}.$$

The constitutions of acetone and tertiary butyl iodide having been determined (*see later*), that of tetramethylmethane is fixed, and, since the reduction of butyl iodide yields *isobutane*, the constitution of the latter is proved.

HEXANES, C_6H_{14}

The five isomeric hexanes which should exist are all known (*see* Table, p. 32). They are found particularly in *petroleum ether*, *gasolene*, and *ligroin* (*i. e.*, in the portions of petroleum boiling below 150°), together with *heptanes* and *octanes*. They are formed also from shaly coal like cannel coal and boghead.

HIGHER HYDROCARBONS

These are very numerous and are found in petroleum and in its residues (vaseline, paraffin wax, etc.); they distil unchanged (after C_{16}) only in a vacuum, the boiling-point being thus lowered by about 100°.

Many of these higher normal hydrocarbons were prepared synthetically by Krafft by reducing the corresponding fatty acids, alcohols, and ketones. They are generally soluble in ether, petroleum benzine and, partly, petroleum itself, but are insoluble or almost so in alcohol, acetone, acetic acid, acetic anhydride, etc.

HEPTACOSANE, $C_{27}H_{56}$, and **HENTRIACONTANE**, $C_{31}H_{64}$, are found in beeswax and in American tobacco (about 1 per cent.), the former being also found in soot.

HEXACONTANE, $C_{60}H_{122}$, is the highest term of the paraffin series to be prepared synthetically by Hell and Hägele in 1889 by condensing 2 mols. of myricyl iodide, $C_{30}H_{61}I$, by fusion with sodium, which removes the iodine as NaI. It melts at 102°, is slightly soluble in alcohol or ether, and distils, to some extent unchanged, in a vacuum. It has probably the normal structure and thus forms the longest carbon atom chain as yet prepared synthetically.

Some of the saturated hydrocarbons of the aliphatic series have important practical applications, especially as sources of light and heat. In illuminating gas are found the gaseous members, in petroleum the liquid, and in paraffin wax the solid ones.

A brief account of the industrial treatment of these three products will now be given.

ILLUMINATING GAS[1]

Illuminating gas and the other products of the dry distillation of coal vary in composition with the nature of the coal employed. In gas manufacture, account has to be

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[1] **History.** This industry began with the nineteenth century, its apotheosis being reached at the end of that century with the application of the incandescent gas-mantle. From the year 900 the Chinese have employed petroleum vapour, distributed by wooden pipes, for lighting purposes. It was, however, only in 1739 that James Clayton, in investigating the causes of the emanation of inflammable gas often occurring in the Lancashire mines, heated coal in closed vessels and collected the gas (illuminating gas !) developed in large bladders. In 1767, Watson, in laboratory experiments on a small scale, obtained gas, ammonia, and coke by the distillation of coal. This was the time when coke was beginning to be employed in metallurgical operations, and in 1786 Lord Dundonald used the gas from the coke furnaces to light his house, and Pickel lighted his own laboratory with the gas formed on distilling bones. More important trials were, however, made in Great Britain by W. Murdock (or Murdoch), for the illumination of large works by distilling coal. Helped in his undertaking, first by Watt, the inventor of the steam-engine, and afterwards by his pupil Clegg, he succeeded in 1805 in extending lighting by gas to many establishments. The distillation of wood was studied by the engineer Lebon, in France, and in 1799, a patent was taken out "for a new method of employing fuel more efficiently, for heating or lighting, and of collecting the various products." Some days later, all Paris was admiring the gas-lamp which Lebon used to illuminate the gardens of the Hôtel Seignelay. Probably Lebon did not then foresee the wonderful development which was to take place in gas lighting in the nineteenth century, or dream of the monument to be erected to him many years later in his native town, Chaumont, or of the statue which was dedicated to him in Paris in 1905.

It was when the use of large plant was attempted for lighting by gas that technical difficulties cropped up, inconveniences which were negligible on a small scale becoming insurmountable in the case of large works. It was already noticed that the new illuminating gas burned with a rather sooty flame and disseminated unpleasant odours, whilst in the works the piping often became obstructed owing to solid distillation products being carried by the gas. If, in addition, we consider the popular prejudice to any innovation, aggravated by the fantastic propaganda of certain scientific men, especially in France, who exaggerated the danger of explosion, it is easy to conceive how unpromising the conditions of this industry were up to 1812. To Clegg is due the elimination of the main technical difficulties, the tarry matters carried along by the gas being removed by means of a number of cooled tubes, and further purification being effected by lime, the gas being then collected in large gasometers, from which it was distributed by pipes to the consumers. Thus, it became possible in 1813 to light part of London with coal gas, and in 1815 Winsor illuminated certain quarters of Paris. In 1816 Bartolomeo Bizio lighted the portico of the Academy of Fine Arts in Florence with gas distilled from wood.

Nobody on the Continent dared attempt a similar industry; everybody was distrustful, not foreseeing its great future and being frightened by the technical difficulties which met this, the first great chemical industry, which was thus for many years confined to England. It was in this country that it underwent the most rapid extension and perfection (in 1823, fifty-two towns were lighted by gas), the scientific and practical men giving it their entire support. In 1810 a powerful English company was founded by Clegg and became later the famous Imperial Continental Gas Association, which, with a capital of £2,000,000 in 1824, £3,500,000 in 1874, £3,800,000 in 1897, and £5,000,000 in 1908, was formed with the view of undertaking the lighting of the principal European towns. Even to-day many towns are still pledged to contracts, as yet unexpired, with the great English companies. London itself, within the last few years, has found the greatest obstacle to the introduction of electric lighting in contracts with gas companies which have already made fabulous profits.

In Germany, the first small gas-plant was that of Lampadius in 1816, used for his own establishment, extension being subsequently effected as a result of the work of Flashoff and Dinnendhal. At Berlin the first attempt was made in 1826; then followed Hanover, and in 1884, 557 German towns were lighted by gas, the annual consumption of coal being 1,700,000 tons. In Austria the first plant was erected in 1818 by Prechtl. In America, Baltimore was illuminated by gas in 1806, Philadelphia in 1822, and New York in 1834. At Milan gas lighting was introduced in 1832.

After 1870 all the principal populous centres and even the small towns were lighted by gas, all objection to this form of illumination having disappeared; experience had shown that the expected terrible explosions of mixtures of gas and air did not occur, and that the small accidents which did happen were not more serious than those occurring daily with paraffin lamps. The taken of the value of the by-products: coke, tar, ammonia, etc., which sometimes contribute largely to the cost of manufacture. Consequently, mixtures of coal are used which give good coke, the luminosity of the gas from certain coals being supplemented by mixing with others rich in hydrogen and bitumen, such as some English coals, like *cannel coal*, *boghead*, various shaly coals, etc.; these are, however, very expensive and have not been used during recent years, since the luminosity is now obtained by means of incandescent mantles (Auer). In general, coals used for making gas have percentage compositions varying between the following limits: C, 78 to 85; H, 5 to 8; O, 6 to 13; N, 1·2 to 1·9; and S, 0·1 to 2, a higher content of sulphur being harmful; they should leave little ash on burning, and preference is given to those yielding considerable quantities of volatile products. The more hydrogen there is, the greater will be the useful yield, since every kilogram of hydrogen can gasify 4 to 5 kilos of carbon (according as more or less methane, ethylene, etc., is formed). Gas-coal giving good coke contains more than 15 per cent. and less than 35 per cent. of volatile products.

The *oxygen* present in coal gives rise to larger or smaller quantities of carbon dioxide and monoxide, the latter being a powerful poison (*see later*, p. 58). Only 10 to 15 per cent. of the *nitrogen* present in the coal is transformed into ammonia, 20 per cent. being found in the gas and 60 per cent. in the coke, whilst 2 to 3 per cent. forms hydrocyanic acid and cyanides in the gas and tar. *Moisture* in the coal is harmful, since water causes an increase in the amount of carbon dioxide in the gas and also absorbs heat for its evaporation.

In order to judge of the value of the coal, distillations are carried out, in gasworks, in small laboratory retorts containing a weighed quantity of coal and heated at a very high temperature (900° and even higher); the gas and vapours are washed in bottles, first with lime-water and then with lead acetate, the pure gas being collected in a cylinder over mercury, so that it may be measured and its composition and illuminating power investigated. In general the laboratory test gives a yield of gas somewhat lower than that obtained in the large works retorts, since in the latter the tar also undergoes partial decomposition and gasification; in laboratory tests it is, therefore, necessary to raise the temperature very gradually and to heat strongly only at the end.

To judge of the practical value of a coal, use is made of the product of the yield of gas (that is, the number of cubic metres from 100 kilos of coal) and its candle-power. For any given coal, this product is almost constant, increase of the temperature of distillation resulting in a greater yield of gas, but of a lower illuminating power. Naturally this rule holds only between certain limits of temperature, which are never exceeded in practice.

Of various coals, the best is that which gives the highest value for this product, but account must also be taken of the yields of coke, ammonia, and tar, and of the specific gravity of the gas.

The temperature of carbonisation varies with the nature of the coal, and, in general, with fatty coals (bituminous) the evolution of gas begins at 50°, and at a red heat vapours of liquid products pass over; at a higher temperature, gaseous products predominate.

The most convenient temperature usually lies between red heat (cherry-red) and yellowish white heat. In general, after an hour's heating (with a furnace at 1400°), the coal in the retort reaches 400°, after three hours 950°, and after five hours 1075°. On heating 1000 kilos of English coal at different temperatures the following results are obtained:

	At dull red heat.	At bright orange red.
(*a*) Gas obtained (cubic metres)	234	340
(*b*) Candle-power	20·5	15·6
(*c*) Candles per 1000 kilos = $a \times b$	4800	5300
(*d*) Composition: Hydrogen	38·1%	48 %
Carbon monoxide	8·7%	14 %
Methane	42·7%	30·7%
Heavy hydrocarbons	7·6%	4·5%
Nitrogen	2·9%	2·8%

Gas prepared at a higher temperature has a lower calorific power.

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victory over petroleum, although furiously contested, was especially complete in the case of public lighting.

To this success have contributed, most of all, the incessant improvements of methods of manufacture which have resulted in the supply of a purer, more abundant, and more economical gas.

The composition of gas varies also according as the heating is more or less prolonged.[1] It will be seen that the diminution of luminosity is less proportionally than the increase in volume of the gas, and to-day the distillation is pushed to a temperature of 1100° to 1200°, this resulting in greater (absolute, not relative) quantities of light, luminous hydrocarbons and of hydrogen being obtained. It is hence important to employ suitable mixtures of coals, so that these may be impoverished as much as possible at a high temperature, the relatively low luminosity being compensated for by the addition of special fatty coals, as already mentioned, and also, at the present day, of benzene.

The duration of the distillation varies from three to five hours; the extra amount of gas that would be obtained by heating further would be insufficient to make up for the cost of heating. Further, less and leaner *coke* is obtained; nowadays the tendency is to produce a coke containing at least 8 per cent. of volatile products, since this burns more easily for domestic heating. One hundred kilos of Westphalian coal give about 71 kilos of coke, 4 kilos of tar, 5 kilos of ammonia liquors, and 17 kilos (30·5 cu. metres) of gas; loss, 3 kilos.

The **COMPONENTS OF ILLUMINATING GAS** obtained from coal are very varied and may be embraced in three groups: (*a*) H, CH_4, CO; (*b*) *light-yielding gases and vapours:* ethane, ethylene, butylene, acetylene, crotonylene, allylene, pentylene, benzene, toluene, xylene, thiophene, styrene, indene, naphthalene, acenaphthene, fluorene, propane, butane, pyridine, phenols; (*c*) *inert or harmful impurities:* CO_2, NH_3, HCN, SH_2, CS_2, COS, N, etc. Naturally the majority of these substances are present only in traces.

The *percentage composition by volume of the gas* usually varies between the following limits: CO_2, 1·25 to 3·20; CO, 4·5 to 6·5 (for English coals, 6 to 9, and for German coals, occasionally 9 to 11); H, 42 to 55; CH_4, 32 to 38; N, 1 to 3; O, 0 to 0·5; aromatic hydrocarbons (benzene, etc.), 0·8 to 1·4; unsaturated hydrocarbons (ethylene, 2 to 2·5; acetylene, 0·1 to 0·2; propylene, 0·2 to 0·5, etc.). The *specific gravity* of gas varies from 0·350 to 0·550 (air = 1) and 1 cu. foot of gas weighs rather more than half an ounce.[2] The *calorific power* of illuminating gas ranges, as a rule, from 4000 to 5000 cals. per cubic metre, thus producing the same heating effect as 3·4 kw.-hours. One cu. metre of gas requires for its complete combustion about 5·5 cu. metres of air (less if mixed with water-gas, 1 cu. metre of this needing only 2·3 cu. metres of air).

In addition to the lighting power (*see later*, p. 62), for which it is mostly used, to the heating power, which makes it a valuable source of mechanical energy for gas engines (*see* p. 60), to the relatively low specific gravity, which renders it useful in aeronautics, attention must be paid to the explosive properties of illuminating gas when mixed with air (*see* p. 34), and to its poisonous properties even when present in only 2 per cent. by volume. Its poisoning

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[1] Wright analysed the gas for three different periods, starting from the beginning of the distillation, and V. B. Lewes (1911) analysed the gas generated at 500° and at 1000°, the results being:

	After 40 minutes.	After three hours.	After six hours.	At 500°.	At 1000°.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
H_2S	0·4	0·78	0·38	—	—
CO_2	2·08	1·34	0·59	2·5	1·1
CO	4·52	6·73	7·52	7·3	6·2
CH_4	56·46	37·46	14·61	48	13
H	25·36	48·36	71·94	27·5	71
Heavy hydrocarbons	8·51	3·13	2·78	13·5	7
N	2·37	2·20	2·18	1·6	1·7

[2] By passing ordinary gas into a retort filled with coke at 1200° or a higher temperature, a new gas, deprived of heavy hydrocarbons, oxygen, and carbon dioxide, very poor in methane (6 per cent.), rather richer in carbon monoxide (7 to 8 per cent.) and very rich in hydrogen (up to 84 per cent.) is obtained. This new gas can be used for aeronautical purposes, its specific gravity being about 0·23 (*Continental Gas Gesellschaft*, Dessau, 1910. *See also* note, p. 58).

effect is due especially to the carbon monoxide present (*see* pp. 43, 58), but also, to some extent, to other components. When the first symptoms of poisoning are observed, fatal consequences may be prevented by vigorous respiration of pure air or, better, oxygen, while the use of compressed air according to Mosso's system also gives good results (Vol. I., p. 190).

RETORTS. Murdoch's first retorts were of cast-iron, placed vertically in a furnace (Fig. 44), but as it was inconvenient to charge them Murdoch introduced inclined retorts (Fig. 45), which he changed later into horizontal retorts of cast-iron (Fig. 46).

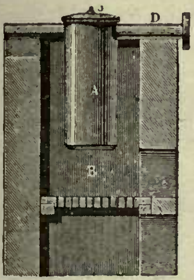

Fig. 44.

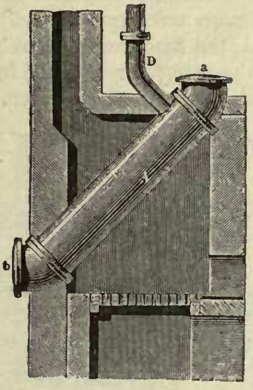

Fig. 45.

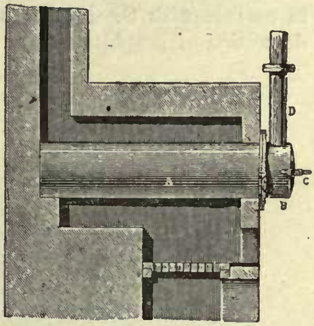

Fig. 46.

In 1820 J. Grafton suggested the use of horizontal retorts of fireclay, since these resist heat better, cost less, and last longer. The most convenient form was that with a ⌓-shaped or elliptical section (Fig. 47), and the most suitable dimensions for these horizontal retorts were found to be: width of the mouth, 43 to 53 cm., height at the middle, 31 to 38 cm., and length, 2 to 3 metres. One end was closed and the mouth was swollen at the edge, which carried screws serving to fix the metal cover fitted with the delivery tube. These retorts were charged, according to their capacity, with 100 to 200 kilos of coal, broken into uniform lumps. Various mechanical connections were devised to allow of the retort being charged and discharged rapidly and with the least expense for hand labour, and one of the best arrangements, with a battery of retorts placed in furnaces over gas producers, is that shown in Fig. 48. However, since 1890 it has become general in the principal European towns to use inclined retorts of elliptical section, which were suggested anew by Coze and are furnished with two mouths projecting from the two ends of the furnace (double-ended or "through" retorts). When these are inclined at an angle of 32° and are charged automatically from above, the coal distributes itself in a layer of uniform depth along the whole of the retort (Fig. 49). The gas-discharge tube is inserted at the lower mouth, which at the end of the operation is opened, the coke, while still hot, being completely and immediately discharged into an iron truck or on to a moving endless perforated band, the pieces of coke remaining alight being sprinkled with water before being discharged on to the coke ground. Similar retorts are used with elliptical mouths; the upper one is rather larger (63 cm. × 35 cm.) than the lower (57 cm. × 30 cm.), and the length is about 3·8 metres. At the present day they vary from this length up to 6 metres.

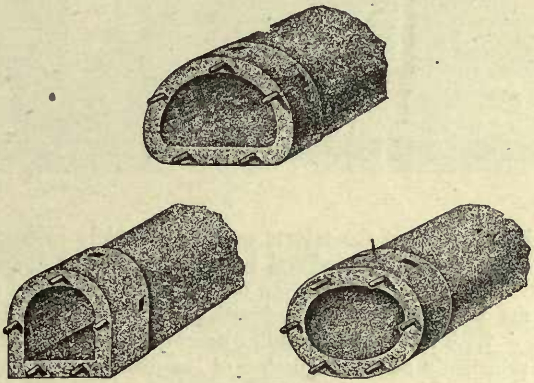

Fig. 47.

The advantages of this system are shown by the following results, which refer to three batteries of fourteen (1) inclined and (2) horizontal retorts :

	Inclined.	Horizontal.
Duration of the distillation	3 hours	$4\frac{1}{2}$ hours
Charge per retort	165 kilos	152 kilos
Number of charges per 8 hours	112	72
Total coal distilled in 8 hours	18,500 kilos	11,000 kilos
Cost of labour per 1000 kilos of coal	10 pence	18 pence

The *pressure* in the interior of the retorts should be carefully regulated, since, if it becomes too great, escape of the light gases and vapours readily occurs and the development of vapours and gases is slackened, the hydrocarbons, which remain for a long time in contact with the red-hot walls of the retort, undergoing further decomposition with deposition of graphite on the walls and liberation of hydrogen. In order to avoid these inconveniences the retorts are to-day put in indirect communication with aspirators or pressure regulators placed beyond the washing apparatus (scrubbers, etc.).

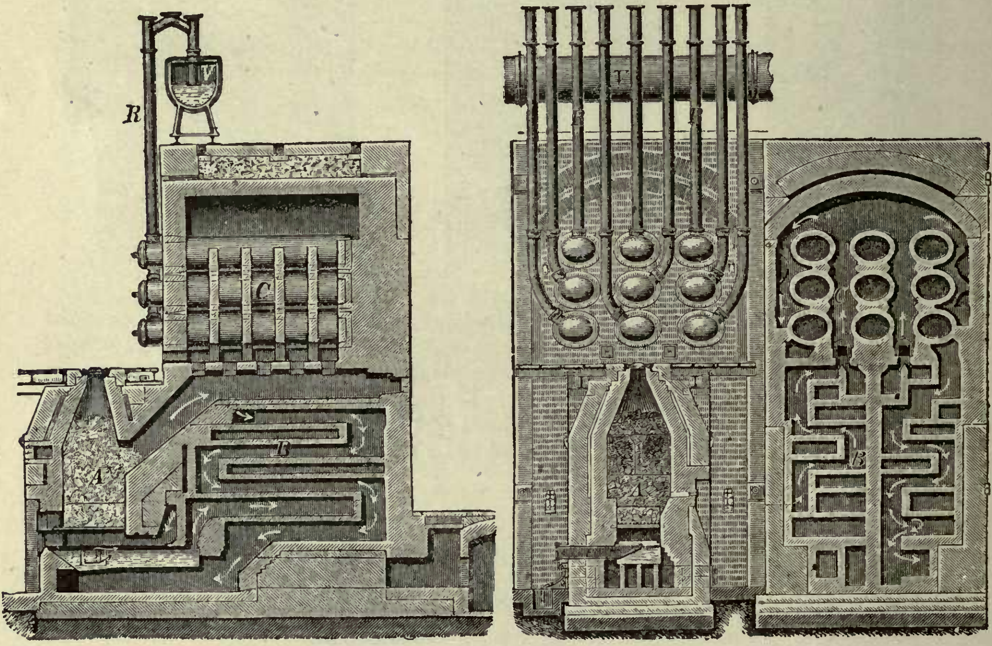

Fig. 48.

The layer of coal in the retort should not be too deep, as otherwise the gases given off are decomposed on contact with the upper layers of hot coke.

With the view of avoiding decomposition of the more luminous gases, which are evolved principally at the beginning of the distillation, Bentrup (1903) proposed passing a continuous current of *water-gas* (*see* Vol. I., pp. 365, 486) into the retort to remove these products rapidly from contact with the hot walls of the retort; the water-gas is produced in an adjacent retort also containing red-hot coke.

As often happens in other fields of work, so also in the industries, a return to older methods often offers advantages. Thus it appears at the present time that the vertical retorts again brought into use by Settle and Padfield are destined to supplant the inclined ones. In 1905, J. Bueb made works experiments with a battery of ten retorts, 4 metres in length, placed vertically in a furnace and provided with an upper aperture for charging and a lower one for discharging (that is, the furnace surrounds only the external vertical surface of the retort, which is heated by hot gases circulating through numerous channels, as shown in Fig. 50). In this way a larger charge (up to 500 kilos) is used, the luminous gases are not decomposed and the yield of gas is higher, as the temperature of the retort reaches 1300° to 1400° C.; at the same time very little naphthalene is produced, the inconvenience caused by depositions of naphthalene in the cold parts of the pipes being thus avoided. In addition, the yield of ammonia is increased by 35 per cent., the separation of the tar is facilitated, and the cost of labour diminished; a less amount of a harder coke is obtained, and the quantity of tar is considerably decreased, while the production of gas is increased (Ger. Pat. 155,742). Further, the tar is more fluid and brown, and differs in composition from ordinary tar, containing only 2 to 4 per cent. of free carbon in place of the 20 per cent. or more in other tar (*see* Tar), and also only one-half as much naphthalene.

Fig. 50 shows a double battery of Bueb vertical retorts, 4 metres high and slightly conical in shape, the wider mouth at the bottom. By means of the elevator, *A*, the coal is introduced into the hopper *B C*, whence it passes into the movable scoops, *D*, which carry it to the retorts. At the end of the distillation (which lasts seven to eight hours) the coke is discharged into the metal hopper *F*, and thence into the channel, *G*, where a band running on rollers carries the spent coke to the store. The gas issues at the top of the retort, and by the tubes *E* and *H* passes into the hydraulic main, *I*, and so into the piping, *L*; the tar and the ammonia liquors are discharged from the hydraulic main into the tube *M*, leading to the depositing tank.

In order to increase the yield of gas by 10 to 15 per cent. it has recently been proposed to utilise the high temperature of the coke (1200° to 1400° C.) remaining in the retorts at the end of the distillation to produce a certain quantity of water-gas by passing a current of steam in at the bottom of the retort for an hour. It cannot, however, be denied that by this *wet process* the proportion of carbon monoxide in the gas is increased (*see* p. 58). In any case total yields of 360 cu. metres of gas per 1000 kilos of coal have been obtained in this way.

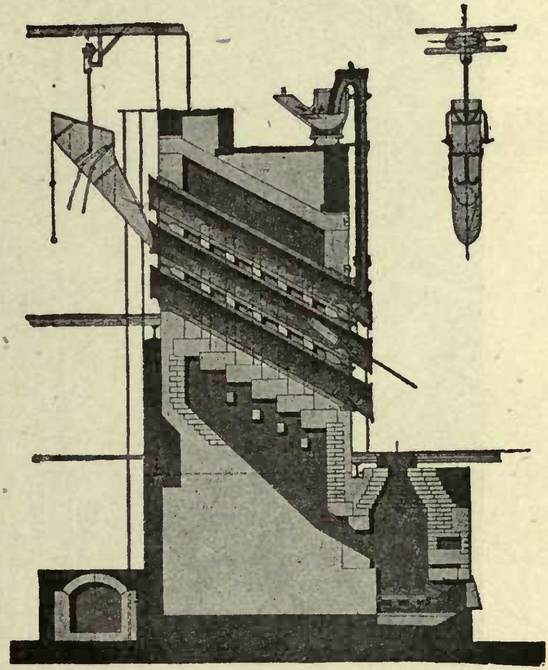

Fig. 49.

The economy in labour effected by this retort is very great, and it is calculated that, whilst with horizontal retorts every workman produces about 1600 cu. metres of gas per day, with the vertical retorts the amount reaches 7000 cu. metres.

From 1906–1910 furnaces with 507 batteries of 5500 vertical retorts, representing a total daily production of 2,200,000 cu. metres of gas, have been manufactured by one single firm at Dessau (for Berlin, Cologne, Zurich, Trieste, Genoa, etc.).

In the working of these vertical retorts, which do indeed represent a marked advance on the Coze inclined retort, certain disadvantages have been observed, the coke formed being harder than the ordinary and not so well suited for domestic purposes, whilst the gas-discharge tubes soon become obstructed with tarry matters, so that they require cleaning every three to four days; distillation with steam during the last phase of the heating relieves this inconvenience to some extent. By some the production of water-gas as described above is not regarded as advantageous, the same quantity of water-gas being obtainable more economically with special plant.

A further and more recent modification consists in the use of *chamber furnaces* (similar to those for making metallurgical coke, *see* Vol. I., p. 453).

At Munich in 1908 and at Vienna in 1909 *inclined chamber furnaces* were employed

(Kopper system, Fig. 51). Coal from the hopper, 2, passes down an inclined plane and fills the chamber, 5; the gas is led into the trough, 1, the coke is discharged, by opening the large lower door with a crane, 4, on to an inclined plane, and so to the chain transporter, 6, and the gas-producer, 8, passes the gas to the dust-chamber, 7, and then to the ascension pipes under the chambers; 9 shows another battery of inclined chambers. With chamber furnaces a better gas is obtained with a less expensive plant and a decided economy in labour, the daily yield of gas per workman reaching 9000 cu. metres; the coke consumed in the producer to heat the furnaces amounts to 13 to 17 per cent. of the coal distilled. A plant of this kind was finished in 1910 at Padua, while one was erected in 1908 at Munich and another in 1912 at Vienna, where the heating of the chambers is effected by gas from a central generator with a revolving hearth (*see* Vol. I., p. 491).

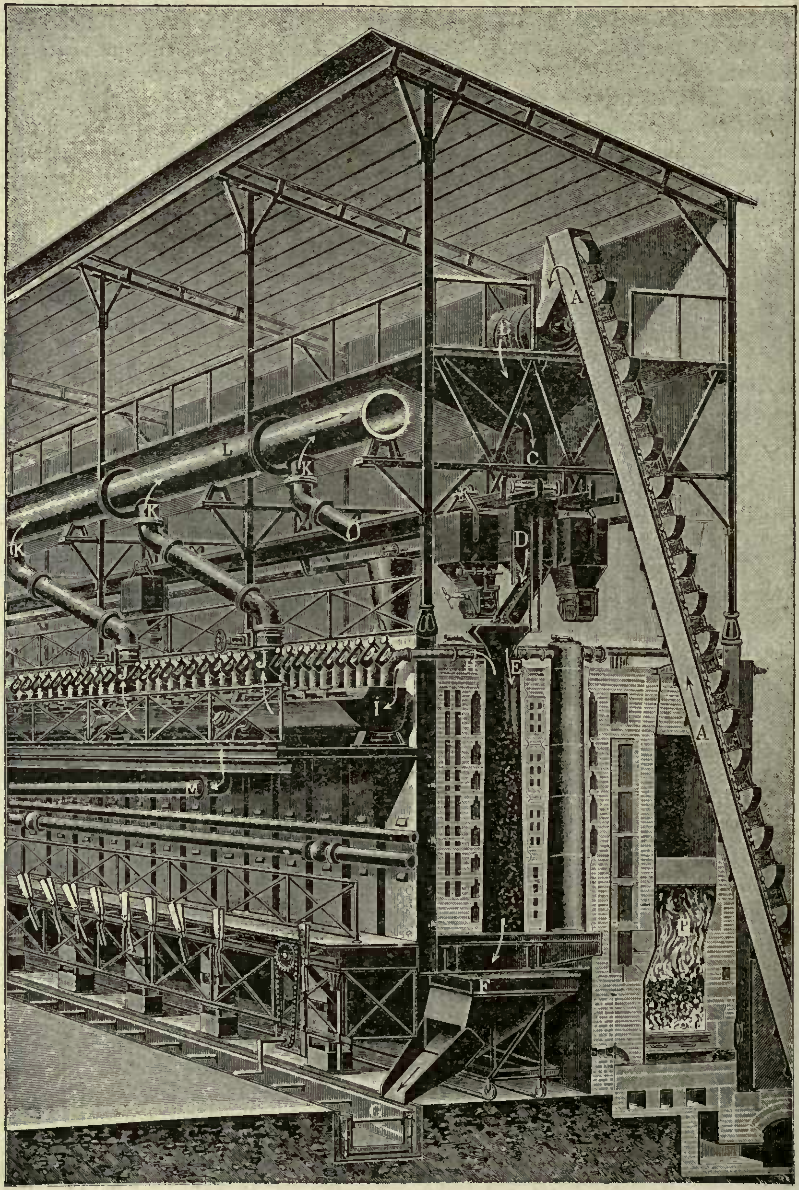

Fig. 50.

With horizontal or inclined retorts the coal is heated for four to six hours; with vertical ones, twelve hours; and with chamber furnaces, twenty-four hours.

FURNACES. Retorts were first of all heated by direct flame, but in this way the heat is inefficiently utilised; then indirect heating by flues, just as for steam boilers, was tried, but the nearer retorts wore out very rapidly, so that later several retorts were placed in one furnace in direct contact with the hot gases, these being so interrupted and deviated that the surfaces of all the retorts were uniformly heated (Fig. 48).

At the present time the use of the *regenerator gas furnace* (*gas-producers, see* Vol. I., pp. 487, 634) has become general, coke (usually waste) being employed, and, in countries where there is little demand for tar, the latter being used as fuel by injection into suitable furnaces. The coke used to heat the furnaces represents about 25 per cent. or 30 per cent. of the total amount produced. In some works (*e. g.*, at Turin since 1909) the heating of the furnaces is profitably effected by 9 to 10 per cent. of tar (on the weight of coal distilled), burnt in special gas-producers with recovery of the heat.[1]

The wear of the furnaces and retorts is considerable, and their cost is calculated as annual expenditure rather than as cost of plant, since they are sometimes remade or renovated twice a year.

PURIFICATION OF GAS. The crude products obtained directly from the carbonisation of bituminous coal cannot be used immediately for lighting and other purposes. The gas issues from the retorts at very high temperatures (up to 250°), and it is evident that, as it gradually cools, various products separate, first of all those which are solid or liquid at ordinary temperatures. It is necessary to remove the tar, naphthalene, ammonia liquor, and the cyanogen and sulphur compounds by means of the following apparatus.

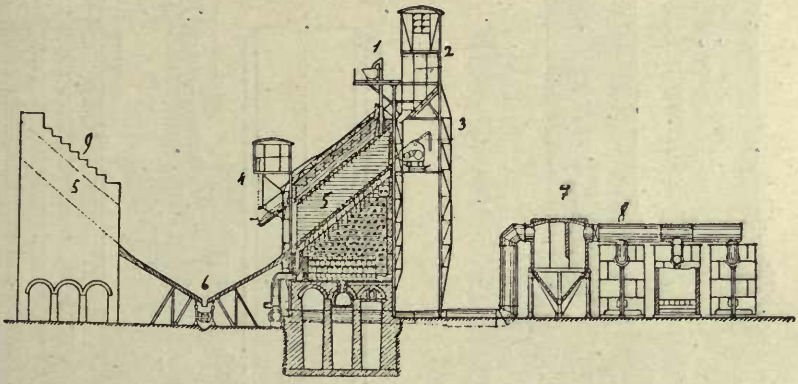

Fig. 51.

HYDRAULIC MAIN. This is a wide circular or semi-circular pipe (diameter, 30 to 60 cm.) of sheet-iron or cast-iron (Fig. 48, *V*), containing water and tar, and placed above the retorts so that the ascension pipes, *R* (12 to 18 cm. in diameter), from one battery of retorts dip into it, these pipes starting from the lower parts of the retorts and carrying off all the hot gas developed. The pipes, *R*, are sealed hydraulically by dipping into water in the hydraulic main, in which most of the tar and the part of the ammoniacal liquor containing the ammonium sulphate, chloride, and thiocyanate condense, while the ammonium carbonate and sulphide condense in the "Standard" (*see below*). The hydraulic main falls slightly towards one end, so as to facilitate flow of the tar to the store-tanks, in which it

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[1] The thermal balance for the distillation of coal is established from the following data: the formation of coke is more or less endothermic according to the higher or lower content of oxygen and volatile products; with less than 3 per cent. of oxygen the endothermic effect is almost zero, and with 7 to 8 per cent., 250 Cals. per kilo of coal. The distillation of such a coal in retorts absorbs 257 Cals., the hot gases and vapours evolved carry away 180 Cals., and the heat remaining in the hot coke is 246 Cals., the total for the retorts alone being 683 Cals. Allowing for the heat radiated from the furnaces and that lost in the gases and ash, the total endothermic effect amounts to 1047 Cals. If the heat of the furnace gases is recovered to heat the air for burning the gas from the gas-producers, the 22 per cent. of coal (calculated on that distilled) consumed in the gas-producers becomes reduced to 10·2 per cent. Good furnaces are those of the Woodall-Duckham and Glover-West types with continuous working.

gradually becomes almost entirely separated from the ammonia liquors, being sold to the tar-distiller with a content of not more than 5 per cent. of water at a price of about seventeen pence per cwt. (3·50 lire per quintal).

The still very impure gas, holding in suspension large numbers of tar drops—which render difficult the condensation of the naphthalene—and having a temperature of 60° to 100° C., is gradually cooled to 12° to 15° C. by causing it to traverse a large iron pipe passing round inside the whole of the works and cooled by the air; the gas then reaches a condenser, formed either of a battery of tall iron tubes (Fig. 52) sprayed outside with water, or of a series of three or four double-jacketed cylinders, 5 to 6 metres high, cooled inside and outside by the air, the gas passing into the jacket (Fig. 53); or the gas may be circulated round a number of narrow tubes through which passes a continuous stream of cold water (Fig. 54). The cooling thus effected is gradual, and the separation of the naphthalene and tar is more complete, while there is no danger of stoppages from the naphthalene; in winter the gas enters the cooler at 50° to 60° C. and leaves at 5° to 10° C., while in summer it enters at 60° to 70° C. and emerges at 30° to 35° C. At the bottom of these tubes is found a deposit of tar—which is discharged into tanks—and of ammonia liquors at 7° to 8° Bé. The consumption of water in these coolers is from 3 to 4 cu. metres per twenty-four hours per 1000 cu. metres of gas.

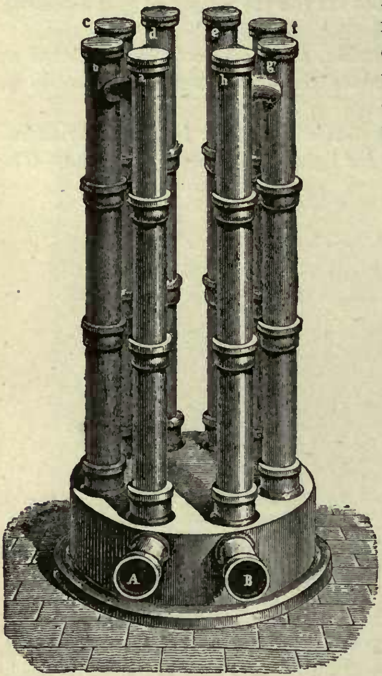

Fig. 52.

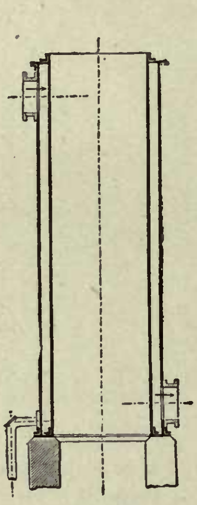

Fig. 53.

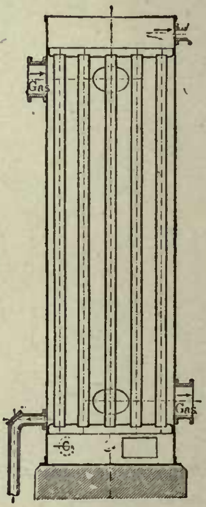

Fig. 54.

If an obstruction of naphthalene occurs at any point, the pressure—indicated by manometers placed along the tubes—shows an increase at that point.

The gas issuing from the condensers still contains suspended tar, which it is necessary to separate. To this end serves Audouin and Pelouze's tar-separator, shown in Fig. 55. The gas passes along the tube *B*, which opens into a perforated double-walled bell, *D*, the pressure in which is regulated by a compensating weight and pulley, *G*. The bell is partially sealed hydraulically and rises more or less, leaving open a greater or less number of apertures, according to the pressure of the gas. The gas is thus subjected to a kind of filtration through small orifices, the fine drops of tar being condensed into larger drops, which separate and collect in *E*, whence the excess is run off at *F*. The gas thus purified from tar passes by the tube *C* to the ammonia-condensing apparatus. The tar-separator should not be kept too cold (12° to 15° C.).

NAPHTHALENE SEPARATORS. Naphthalene is a product of the condensation by heat of the heavy hydrocarbons of the gas. It is difficult to imagine how pertinaciously gas carries through all the purifying operations considerable quantities of naphthalene suspended in it, and how slowly this naphthalene is deposited in town mains, ultimately stopping them and causing great inconvenience and expense to consumers and manufacturers.

In 1899 Bueb, on the basis of former experiments of Young and Glover, succeeded in avoiding this trouble to a great extent by passing the gas (first washed with water in the "Standard" washer-scrubber to separate the ammonia) into a drum similar to the "Standard" (*see below*), but with three independent chambers in which the gas is washed with anthracene oil of medium density (prepared by the distillation of tar and having the b.-pt. 350° to 400° C.),[1] which dissolves and fixes almost all the naphthalene. When the oil of the first chamber is saturated it is removed, and that of the second chamber passes into the first and that of the third into the second; the third chamber is charged with fresh oil, containing 4 per cent. of benzene in order to avoid loss of light-giving products from the gas. The anthracene oil, saturated with naphthalene (23 per cent.) may be utilised as such, or mixed with ordinary tar. Less than 5 grams of naphthalene per 100 cu. metres remains in the washed gas.

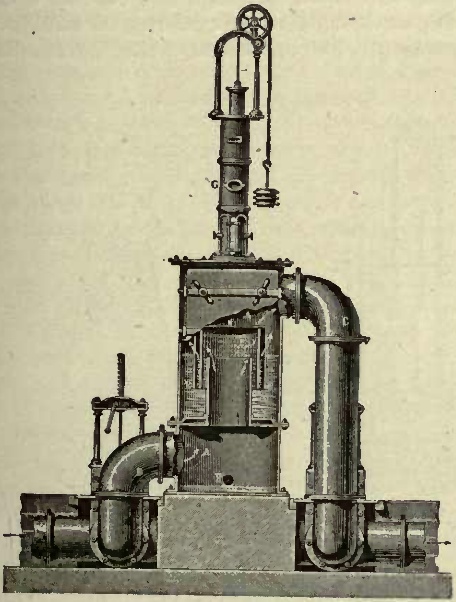

FIG. 55.

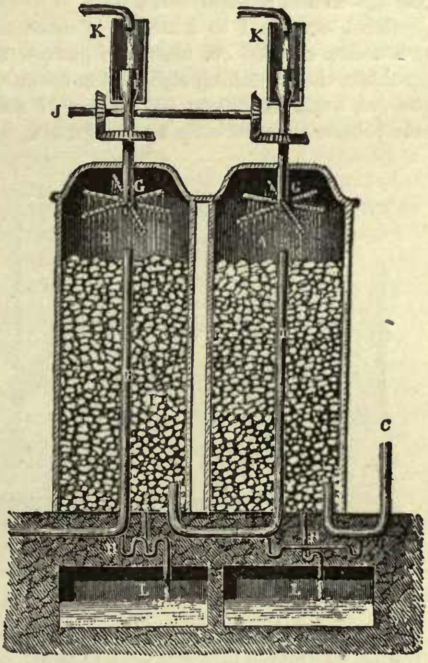

FIG. 56.

According to U.S. Pat. 968,509 of 1910, naphthalene may be separated by bubbling the gas through an aqueous solution of picric acid, this giving rise to an insoluble naphthalene picrate, from which the naphthalene may be distilled by means of steam, the picric acid being left.

SEPARATION OF AMMONIA.[2] The washing of the gas for the purpose of removing

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[1] It seems that, when a lighter tar oil (sp. gr. less than 1) is used in the proportion of 3·76 grams per cubic metre of gas, as much as 0·951 gram of naphthalene can be fixed, whereas the heavy oil fixes only 0·2 gram; in the former case as little as 2 grams of naphthalene per 100 cu. metres has been left in the gas.

[2] Of the nitrogen present in coal (1 to 2 per cent.), about one-half remains in the coke, 2 to 3 per cent. yields cyanides and hydrocyanic acid, and about 20 per cent. occurs free, and 10 to 15 per cent. as free and combined ammonia (ammonium sulphide, carbonate and chloride) in the gas. It has been shown that the proportion of nitrogen transformed into ammonia is much greater than that found in this form in the gas, as more or less of the ammonia undergoes dissociation into nitrogen and hydrogen (especially above 800°). The extent of this dissociation depends on the nature of the ash of the coal (iron and its oxide act as dissociating catalysts in the hot) and on the temperature of the walls of the retort and of the coke. Thus, in horizontal retorts, where the gas remains more readily in contact with the upper walls, which form a heated arch, the ammonia is more highly dissociated than in vertical retorts and in chamber furnaces, where the gas is in contact more with the central mass of the coal than with the retort walls.

the ammonia may be effected by ordinary water, which has a great affinity for ammonia, or by the dilute ammonia liquor from the hydraulic main (1° to 2° Bé.), but not with that from the condenser, which is too concentrated (7° to 8° Bé.). The most common form of apparatus used for this washing is the *scrubber* or, better still, the "Standard" washer-scrubber.

SCRUBBERS are usually formed of a series of coke-towers through which water trickles (Fig. 56). The gas that enters the bottom of the first tower is washed with dilute ammonia, condensed in succeeding towers, and when it reaches the last tower it is washed with pure water, which dissolves the last traces of ammonia and may be used subsequently for the first tower, from the bottom of which it is carried off, rich in ammonia, by small syphons. These towers, which are of cast-iron sheets, are joined in twos or threes in such a way that the gas is conducted from the top of the first tower to the bottom of the second, and so on. The interior may be fitted simply with water pulverisers, or it may be filled with coke, chips of wood, broken bricks, or, what are more efficient, vertical bundles of sticks, or of corrugated and toothed iron sheets.

Scrubbers are 1 to 3 metres in diameter and 4 to 20 metres in height. A maximum production of 1000 cu. metres of gas per twenty-four hours requires 5 to 6 cu. metres of scrubber, the gas taking eight to ten minutes to pass through. Before entering the scrubber the gas contains 200 to 400 grams of ammonia per 100 cu. metres, whilst afterwards this volume contains only 1 to 10 grams.

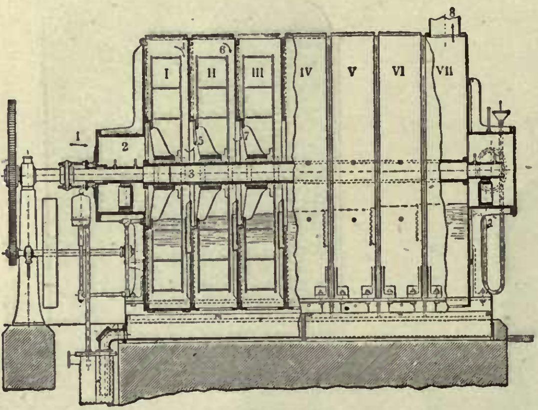

Fig. 57.

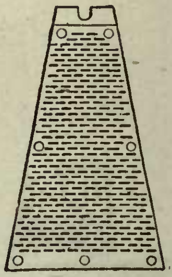

Fig. 58.

The "**STANDARD**" washer-scrubber consists of a large horizontal fixed cylinder of iron-plate, divided by septa normal to the axis into seven chambers (Fig. 57). This cylinder is traversed by a rotatable axis carrying seven paddles of almost the same diameter as the chambers and each consisting of two large metal plates to which are fixed the ends of superposed wooden laths with spaces, not exactly superposed, between (Fig. 58). These paddles rotate with the axis and dip into water which fills the chambers to about one-third of the height of the cylinder. The pure water enters chamber VII at *a* and passes from chamber to chamber until it reaches the first, the walls separating the chambers being successively lower. The gas to be purified moves in the opposite direction, entering chamber I, and passing between all the laths of the paddle from the centre to the periphery, then descending to the centre of the next paddle in chamber II, as shown by the arrows, 4 and 5, again issuing at the periphery, passing into chamber III, and so on. In this way the gas is perfectly washed and loses also part of its CO_2 and H_2S. The water leaves chamber I with a density of 7° to 8° Bé.

At Munich the ammonia is eliminated in the dry way by passing the gas over superphosphate, which fixes it and then serves as an excellent fertiliser (with 7 to 8 per cent. of nitrogen): 1000 kilos of superphosphate are sufficient to purify 32,000 cu. metres of gas (with 3 per cent. of NH_3), the small quantity of thiocyanate (0·5 to 2·5 per cent.) which it contains having no injurious action on plants. N. Caro (U.S. Pat. 952,560, March 22, 1910) cools the gas from coke manufacture to 20° and then passes it through a solution of ammonium sulphate of 29° to 35° Bé. containing 5 per cent. of free sulphuric acid;

ammonium sulphate gradually crystallises out and the gas passes off free from ammonia. Generally, however, ammoniacal liquors are distilled with lime and the ammonia fixed with sulphuric acid (*see* Vol. I., p. 358). Every ton of coal carbonised yields 10 to 12 kilos of commercial ammonium sulphate.

For some years increasing use has been made of the method of fixing the *ammonia* of lighting gas by means of concentrated sulphuric acid so as to obtain directly crystallised ammonium sulphate, as was suggested by Mallet in 1840, by Laming in 1852, and by Brun in 1903, the acid being previously heated to 80° to 85° so that the moisture is not condensed and the acid not increased in volume. The tar could not, however, be completely eliminated beforehand from the hot gas; better results in this direction were obtained in 1905 by centrifuging the gas, and in 1906 Otto expelled the tar by passing the gas into towers or cylinders in which tar was pulverised at the top. When the hot gas is treated, this is taken as it issues from the hydraulic main, the shallow layer of tar which always separates at the surface of the acid in the neutraliser being run off by a pipe; the crystalline sulphate which separates is extracted continuously by means of suitable ejectors (*see also* Fr. Pat. 418,018). In order that water may not condense in the pipes before the neutralising vessel, the gas must be kept at about 80° (gas from coke-ovens contains up to 145 grams of water vapour per cubic metre, and in this case the temperature of hygrometric saturation is 80·7°); the tar separator must also be warm, in order that water may not condense therein. The crude gas may contain 10 to 12 grams of ammonia per cubic metre, and the heat of reaction with sulphuric acid suffices to maintain the temperature of the acid and gas; the heat of reaction is greater for the ammonia existing as salts. If less than the above proportion of ammonia is present and the gas is saturated with moisture, the heat of reaction is insufficient and the acid must be heated. Less convenient is the Koppers' system, according to which the gas is cooled to 30° to separate the tar and then heated by a counter-current of the hot furnace gases, the ammonia water condensing at 30° being heated separately to expel the ammonia which is introduced into the gas before the latter reaches the neutralising vessel.

SEPARATION OF THE SULPHUR COMPOUNDS AND CYANOGEN COMPOUNDS. The volatile or organic *sulphur* of the coal (0·4 to 0·8 per cent. S.) occurs to the extent of about one-half in the impure gas, 97 per cent. of it as H_2S and sulphides and the rest as CS_2 and other aliphatic and aromatic sulphur compounds (*see above*). The *fixed sulphur* of the sulphates and pyrites remains in the coke.

After the ammonia, the following gases must be removed: H_2S, COS, CO_2, HCN, CS_2, thiocyanates, sulphur derivatives of hydrocarbons, etc. This is especially important with H_2S and other sulphur compounds (about 1 to 1·5 per cent. by volume of the crude gas), since they partly burn, forming SO_2, and partly escape unaltered from the gas-jets, decorations, metal-work, and paintings being discoloured; also the poisonous properties of these compounds are considerable, the crude gas containing 0·1 to 0·25 per cent. by volume of hydrocyanic acid. The test employed by large consumers to detect hydrogen sulphide is very rigorous, and is made with lead acetate paper, which blackens on prolonged exposure to impure gas.

The final purification of gas has been in use ever since the beginning of the industry. In 1806 Clegg purified gas partially by passing it through milk of lime, but such large volumes of liquid were required that their preparation was difficult, while the purification effected was not complete. He then proposed the use of powdered slaked lime, which fixes carbon dioxide, as well as many sulphur compounds, forming calcium sulphydroxide, OH·Ca·SH; but if much CO_2 is present the sulphydroxide is decomposed and SH_2 regenerated. In 1840 Mallet suggested the use of manganese oxide, which fixes H_2S more readily, but this method did not give good results.[1]

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[1] In 1847 Laming succeeded in purifying gas well and easily by means of a mixture of 160 parts of lime, 180 of sawdust, and 30 of ferrous sulphate dissolved in scarcely sufficient water to moisten the mass; it is kept turned over for some days in the air, until it becomes brown owing to the conversion of the ferrous sulphate into ferrous hydroxide and then ferric hydroxide. The latter, in the moist state, is capable of fixing rapidly the hydrogen sulphide and the sulphides (*see* p. 50), while part of the carbon dioxide is fixed by the excess of lime. The use of *Laming mixture* spread quickly to almost all gas-works, and only subsequent to 1890 was it replaced gradually by natural hydrated ferric oxide (*see* p. 50).

In 1868 F. C. Hills attempted to separate the sulphur compounds of the gas and those occurring in the ammonia water (especially as ammonium sulphide and carbonate) by washing the gas with this water heated to 90°, since at this temperature these substances dissociate, the

Nowadays the dry purification of lighting gas is effected almost everywhere by means of natural hydrated ferric oxide ($Fe_2O_3 + 2Fe(OH)_3$) in the form of the porous, yellowish-brown earth, *limonite*, which is mixed with a little lime and sawdust to render the reaction less violent. The ferric hydroxide fixes the hydrogen sulphide and other sulphides: $2Fe(OH)_3 + 3H_2S = 6H_2O + Fe_2S_3$ (iron sesquisulphide or $2FeS + S$) with development of heat, and also forms iron cyanide or thiocyanate with the hydrocyanic acid, *i. e.*, with the ammonium cyanide and thiocyanates.

The whole of the iron present does not take part in these reactions, but when the mixture is exhausted it may be regenerated by exposure and turning in the air for two or three days, the whole of the sulphur being liberated:

$$Fe_2S_3 + 3O + 3H_2O = 2Fe(OH)_3 + 3S.$$

The mass may be thus revivified and used again some ten or more times, after which it is rejected. This product contains 35 to 50 per cent. of free sulphur, 10 to 15 per cent. of Prussian blue, 1 to 4 per cent. of ammonium thiocyanate, and 1 to 4 per cent. of ammonium sulphate, and nowadays the free sulphur is often extracted by carbon disulphide, while from the residue cyanides and ferrocyanides may be obtained; or the mass is first extracted with water to obtain the cyanides and the ammonium sulphate, the dried residue being used in place of pyrites in the manufacture of sulphuric acid (*see* Vol. I., pp. 291, 840).[1]

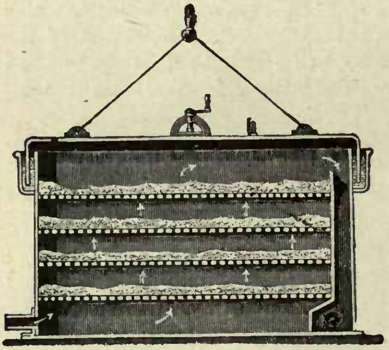

FIG. 59.

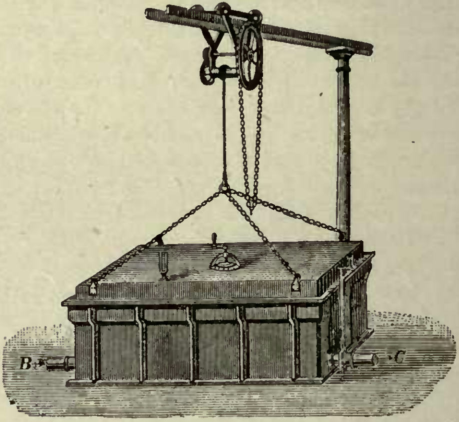

FIG. 60.

These mixtures give good results and are placed on the market under various names: Deicke mixture with 66 per cent. Fe_2O_3 and Lux mixture with 51 per cent. Fe_2O_3. They are made by mixing the powdered iron residues from the working of bauxite with soda and fusing in a furnace, the silicates which have become soluble being then extracted by water and the remaining ferric hydroxide mixed with double its volume of sawdust: 1 cu. metre of this "Lux" mixture, at an initial cost at the Ludwigshafen factory of about 15*s.* per ton, purifies more than 10,000 cu. metres of gas, whilst natural Silesian ferric oxide costs 8*s.* to 12*s.* per ton.

The purifying mixture is arranged in several layers, all of which are traversed by the gas (Fig. 59). The cover to the chamber is water-sealed (Fig. 60), and may easily be raised by means of a crane when the mass is to be removed for regeneration. It is simpler to

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H_2S and CO_2 being liberated and the more soluble ammonia retained; actually, however, a large part of the ammonia is lost, and the process was abandoned. C. F. Claus (1884–1892) applied on a large scale at Belfast the purification of gas from sulphur compounds by using gaseous ammonia instead of aqueous ammonia in a complex system of scrubbers, pumps, heaters, etc., the sulphur of the hydrogen sulphide being recovered in the same way as from Leblanc soda residues (*see* Vol. I., p. 596); the process failed in practice and was discarded.

[1] The cyanogen compounds of the crude gas which are formed from ammonia by the action of heat and cause corrosion of ironwork are best separated in the *wet* way by Bueb's process (Vol. I., p. 840). This process has given satisfactory results in the Turin gasworks and many others in Europe, but is already beginning to lose its importance, owing to the discovery of new synthetical methods of preparing potassium cyanide (Vol. I., p. 548).

use a single layer of the mass 50 to 60 cm. deep, the gas being introduced at a greater pressure; it is then easier to discharge the exhausted mass through an aperture in the base of the reservoir.[1] At the present day the costly labour required for the regeneration is avoided by not emptying the reservoir, the mass being kept always oxidised by mixing about 1·5 to 2 per cent. of air with the gas before passing it into the chamber; with more air the mass heats too much.

Many years ago W. Feld attacked the problem of separating the sulphur compounds from gas. In his first attempts he utilised the ready absorption of H_2S by zinc thiosulphate, with separation of S and ZnS, the latter being afterwards converted into the thiosulphate by means of SO_2: (*a*) $ZnS_2O_3 + 3H_2S = ZnS + 4S + 3H_2O$; (*b*) $2ZnS + 3SO_2 = S + 2ZnS_2O_3$. A plant erected at the works of the East Hull Gas Company in 1909 did not give satisfactory results, and was abandoned in 1910, the conversion of zinc sulphide into the thiosulphate being difficult; further, the regenerated solution absorbs the H_2S less completely (only 30 to 40 per cent.), zinc sulphate being formed.

In the second stage of his attempts Feld used iron thiosulphate, which not only fixes the H_2S more easily, but also completely fixes the ammonia, with formation of FeS (this with SO_2 gives the thiosulphate again) and ammonium thiosulphate; the latter, with iron thiosulphate and SO_2, yields iron and ammonium polythiosulphates: (*c*) $FeS_2O_3 + H_2S + 2NH_3 = FeS + (NH_4)_2S_2O_3$; (*d*) $2FeS + 3SO_2 = S + 2FeS_2O_3$; (*e*) $FeS_2O_3 + (NH_4)_2S_2O_3 + 3SO_2 = FeS_3O_6 + (NH_4)_2S_4O_6$. In the hot these polythionates decompose thus: (*f*) $FeS_3O_6 + (NH_4)_2S_4O_6 = 3S + FeSO_4 + 2SO_2 + (NH_4)_2SO_4$. The final mass thus obtained is also capable of fixing ammonia and H_2S, with separation of ammonium sulphate: (*g*) $FeSO_4 + 2(NH_4)_2SO_4 + 2NH_3 + H_2S = FeS + 3(NH_4)_2SO_4$; with SO_2, the ferrous sulphide yields the thiosulphate (*d*) again.

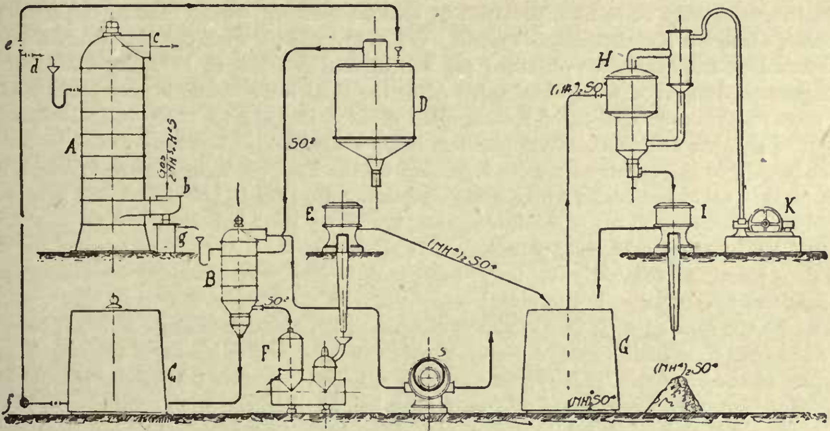

FIG. 61.

This second process of Feld was tried in the municipal works at Koenigsberg, the results being moderately satisfactory, especially if the gas is hot. Feld then found that ammonium polythionate (formed from the thionate and SO_2, *see* reaction *e*) suffices to fix both the ammonia and the hydrogen sulphide: (*h*) $(NH_4)_2S_4O_6 + 3H_2S = (NH_4)_2S_2O_3 + 5S + 3H_2O$; (*i*) $(NH_4)_2S_4O_6 + 2NH_3 + H_2O = S + (NH_4)_2S_2O_3 + (NH_4)_2SO_4$, and, in the hot, (*k*) $(NH_4)_2S_4O_6 = (NH_4)_2SO_4 + SO_2 + 2S$. The sulphur separating is transformed into SO_2 by burning it with air, so that all the ammonia and sulphur of the gas are converted into ammonium sulphate *without using sulphuric acid*. The ammonium polythionate solution is obtained at the beginning of the process from the gas itself, which

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[1] This exhausted mass is often utilised for the sulphur it contains, while in many other cases the cyanides, thiocyanates, ferrocyanides, etc., are extracted (*see* Vol. I., p. 841); it is also sometimes used on roads as a weed-killer—cyanides having a poisonous action on plants—and, finally, it has been proposed as a nitrogenous fertiliser (it contains on the average 5 to 6 per cent. of nitrogen, one-tenth of which is in the form of ammonia and the rest as cyanide), but it must be spread on the naked soil two or three months before sowing takes place, as it takes time to decompose and become innocuous to vegetation.

contains ammonium sulphide (after the Pelouze tar separators), by passing it into the Feld centrifugal washer (*see below*) together with SO_2: $2(NH_4)_2S + 6SO_2 = 2(NH_4)_2S_4O_6$. The Koenigsberg plant is shown diagrammatically in Fig. 61. The ammonium polythionate solution is pumped by the pump *f* from the vat *C* to the upper part of the Feld centrifugal washer *A*, the mouth *b* at the lower part admitting the gas which issues purified from the upper orifice *c*. When the polythionate is converted into thionate according to equations *h* and *i*, it is discharged into a small Feld washer *B*, where it meets a current of hot SO_2 from the sulphur burner *S*, and collects in the *regenerating vat C*, in which the conversion into polythionate is completed. This passes into circulation again until it becomes enriched with 35 to 40 per cent. of ammonium sulphate, part of the solution then going through the tap *e* to the boiler *D*, where it is heated with steam at 100° for five to six hours in order to transform the polythionate into ammonium sulphate with separation of sulphur and formation of SO_2 (*see* reaction *k*), the latter being conducted into *B*. The boiler is then discharged into the centrifuge *E*, which retains the sulphur, whilst the hot ammonium sulphate solution collects in the vat *G*, whence it is delivered into the vacuum evaporator *H*; from this the ammonium sulphate is discharged, as it separates, into the centrifuge *I*, the vacuum in the evaporator being maintained meanwhile by the pump *K*.[1]

At Koenigsberg 40,000 cu. metres of gas are purified per twenty-four hours, with production of 400 kilos of sulphur, which is burnt. The absorption of the ammonia is complete, independently of the temperature of the gas and air, whilst that of the hydrogen sulphide, although not complete, is good. Whereas in 1910, with the old plant, 5·5 kilos of ammonium sulphate were obtained per ton of coal gasified, in 1912, by means of the Feld process, 10·2 kilos were obtained. After the final improvements had been made in the process, the municipality of Koenigsberg decided in 1913 to apply it to their whole output of gas, the old cumbersome purifiers being abandoned. The success of this process is due largely to the excellent results furnished by the Feld centrifugal washer, which may be applied in other industries where gases containing dust are to be washed or where gases, mixed and diluted with other insoluble gases, are to be dissolved and fixed.

This Feld washer (Fig. 62), patented in 1905, consists of five or more superposed cast-iron rings forming a tower divided into as many chambers communicating with one another by means of apertures, *a*, in the plates separating the chambers. A central shaft, rotated rapidly by the gearing *C*, is fitted in each chamber with a cast-iron cross-piece, *b*, to which are fixed four concentric cones of 5 mm. sheet-iron, open at the base and with the smaller aperture at the bottom. These cones are 28 mm. apart, the external peripheral cone being somewhat higher, and perforated all round for a height of 18 cm. with orifices 5 × 12 mm. When the shaft and cones rotate, the liquid of the basin into which they dip is drawn up between the cones and forced out of the mouth at the top, forming a disc of liquid having the diameter of the apparatus; the liquid projected against the walls falls to the bottom,

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[1] Returning to the Hills and Claus process (*see above*) Burkheiser filed a series of patents (Ger. Pats. 212,209, 215,907, 217,315, and 223,713, 1907–1909) according to which the sulphur of the purifying mixture is utilised by converting it into SO_2 by prolonged treatment with a stream of air. The air is then passed into the ammonia water used for washing the gas, ammonium sulphite and afterwards the bisulphite being formed. At this point the crude gas is washed with this bisulphite solution, which fixes the ammonia with formation of ammonium sulphite, this being again treated with the air and SO_2; this process is repeated until the solution deposits ammonium sulphite (less soluble than the bisulphite), which already contains 60 per cent. of the sulphate, formed by oxidation with atmospheric oxygen. By further oxidation in the air the formation of sulphate is almost completed, the residual sulphite being removed by sublimation at a temperature below 100°. Ammonium sulphite, $(NH_4)_2SO_3$, has a pronounced alkaline reaction and exhibits little stability either in solution or in the crystalline state; in the air, and especially in the hot, it gives up ammonia and readily absorbs SO_2 to form the bisulphite: $(NH_4)_2SO_3 + SO_2 + H_2O = 2NH_4HSO_3$. The latter also is unstable and readily loses SO_2, while NH_3 re-converts it into the sulphite: $NH_4HSO_3 + NH_3 = (NH_4)_2SO_3$. Owing to this instability, the fixation of the ammonia with SO_2 according to the equation, $2NH_3 + SO_2 + H_2O = (NH_4)_2SO_3$, is incomplete. This process was improved by Drehschmidt and tested in the municipal gasworks at Berlin. The crude gas was passed in a scrubber through the washing liquid containing the ammonium bisulphite with ferric oxide in suspension, the ammonia being fixed with formation of ammonium sulphite (*see above*) and the hydrogen sulphide with partial separation of sulphur: $Fe_2O_3 + 3H_2S = 3H_2O + 2FeS + S$. When the oxide is exhausted, it is oxidised together with the sulphur in a furnace to regenerate ferric oxide and SO_2: $2FeS + O_7 = Fe_2O_3 + 2SO_2$. This SO_2, mixed with air, is passed into another scrubber charged with the ammonium sulphite solution from the first scrubber; this results in regeneration of the ammonium bisulphite, which passes to the first scrubber, the process being thus continuous. Oxidation of the sulphite to sulphate is effected without a special furnace.

to be raised again, and so on. The gas to be washed enters at the orifice *A*, traverses the spray in each chamber and rises from one chamber to the next above through the apertures *a*, through which the liquid introduced at *D* or *E* passes down; the gas finally issues at *B*. A Feld washer with seven chambers 1 metre in diameter is capable of washing 40,000 cu. metres of gas per day. At Pompey, near Nancy, three Feld washers 6 metres high and 3 metres in diameter were used before the war to wash 3,750,000 cu. metres of blast furnace gases per twenty-four hours.

After removal of the hydrogen sulphide, the gas still contains a certain quantity of *carbon disulphide* (30 to 150 grams per 100 cu. metres, according to the quality of the coal used), which is not easy to separate, and on combustion yields SO_2, this attacking metal. In 1913 Knoevenagel and Reis proposed to eliminate the CS_2 by means of the sodiocellulose from which sodium xanthate is formed (*see later*, Viscose silk), but it is necessary first to remove the CO_2 from the gas (by potassium carbonate, *see* Vol. I., p. 477, and the last traces by lime). The sodium xanthate may be utilised by regeneration of the cellulose by suitable washing and dissolving it in concentrated formic acid to give formylcellulose, which constitutes a substitute for celluloid. Ten tons of sodium xanthate fix the 1·25 tons of CS_2 contained in 100,000 cu. metres of gas. The gas purified in this way still retains a small proportion of sulphur compounds (one-fourth or one-fifth as much as the original CS_2), but these are not H_2S or CS_2, and cannot be eliminated.

After purification the gas passes through large meters to the gasometers, after traversing a glass bell-jar in which is suspended a strip of moist lead acetate paper for the detection of H_2S. Gas well purified contains less than 2 grams of ammonia and less than 45 grams of naphthalene per 100 cu. metres.

In order to diminish the quantity of carbon monoxide in gas, L. Vignon (1911) proposes to heat it over lime and with steam, by which means non-poisonous hydrocarbons are formed (*see* note, p. 58).

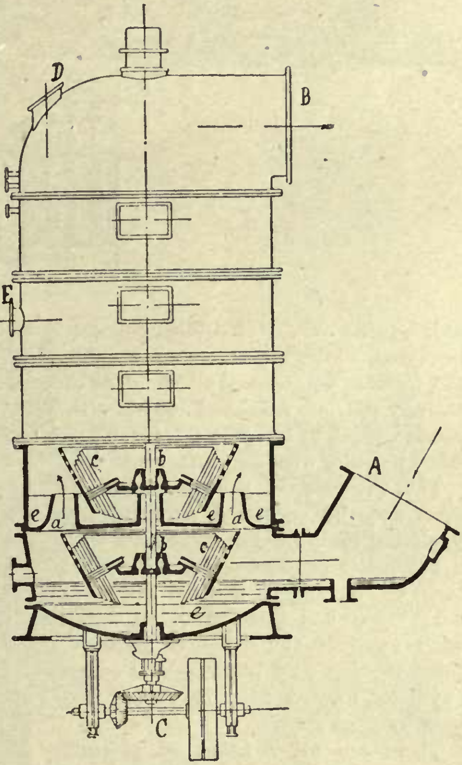

Fig. 62.

EXHAUSTERS. To regulate the pressure of the gas in the retorts and other parts of the plant, exhausters are placed between the condensers and the tar separators, or even after the scrubbers. Sometimes a bell-aspirator is used, consisting of a bell immersed in water and capable of being raised and lowered mechanically, and thus, by means of suitable valves in the lid, of acting both as exhauster and as compressor. There are also piston exhausters, others similar to exhaustion pumps working by eccentrically moving blades (Beale type), etc. The so-called Körting injectors, which make use of steam-jets, are also used as exhausters.

PRESSURE REGULATORS. Since the development of gas cannot be regulated in the retorts, whilst the working of the exhausters is uniform, there may at certain times be an excess pressure generated, especially if the exhausters cease working or the pipes become obstructed. Hence, so-called *pressure regulators* are employed.

To give an idea of one of these simple and ingenious devices, it is shown in Fig. 63 how this regulator is combined with a Körting steam exhauster: *d* is the exhauster, which receives steam from a valved tube, *h*, connected with a bell, *l*, with a water-seal. The gas from the tube a passes through the exhauster to the pipe g. If an excessive pressure develops in the main a, the gas, by means of the tube m, raises the bell l, which in its turn effects a wider opening of the steam-valve and so increases the exhaustion. If the pressure exceeds a certain limiting value, a spring valve or partition in n opens automatically, and the gas discharges also by n into the pipe g.

GASOMETERS. These are formed of large sheet-iron bells fitting one in the other and forming a perfect water-seal when they are inverted in a brick and cement reservoir of water. To economise water, the reservoir is partially filled up by a brickwork cone (termed the "dumpling"), starting from the periphery at the base and rising towards the centre, as shown in Fig. 64; the gas exit and entry pipes project a little above the surface of the liquid. At a certain point (not shown in the figure) these two pipes can be put into direct communication, so that, in case of accident to the gasometer, the gas may still be led to the mains without interrupting the work.

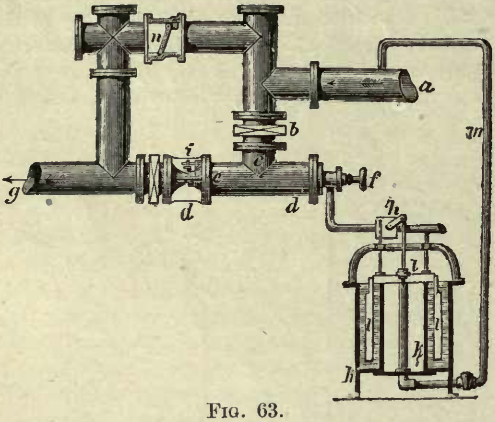

Fig. 63.

To economise in the number and size of the reservoirs and to have gasometers of considerable capacity, so-called *telescopic gas-holders* are now used. These consist of several concentric bells (five or six), of which only the smallest is covered, whilst the others are caught up peripherally during the rising (or filling with gas), forming a water-seal all round, as shown in Fig. 65. In order that the bells may rise centrally they are furnished outside with pulleys running along vertical iron guides. The pressure of gas in the gasometer may be calculated from the weight of the bell outside the water, together with the surface and diameter of the bell itself.

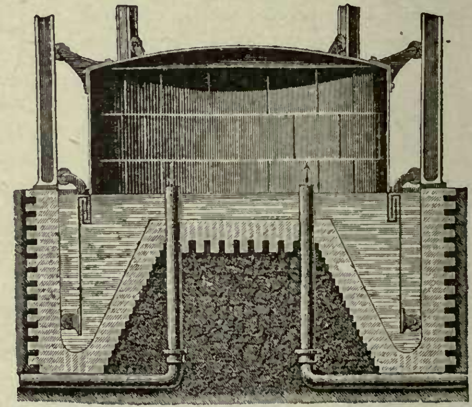

Fig. 64.

The pressure in the gasometer or mains may be registered automatically by placing them in communication with an automatic pressure-measure like that shown in Fig. 66. In this the gas raises or lowers a bell fitted with an index which registers the different pressures during the day on a paper wound round a cylinder rotated once in twenty-four hours by clockwork.

There are other forms of pressure indicators, but the above, although old (in principle), is still largely used, being simple and exact.

In order to avoid the serious consequences contingent on a gasometer reservoir cracking or leaking, iron reservoirs built above ground are now preferred, the slightest escape being then observable and remediable at any moment. Such a *suspended telescopic gasometer* is shown in Fig. 65.

To meet the enormous daily consumption of gas in large cities more and more capacious gas-holders are required—sufficient to contain three or four days' supply and so avoid the inconveniences of an interruption of work (from damage, strikes, etc.). In Milan, prior to 1908, the largest of the gasometers (measuring altogether 150,000 cu. metres) had a capacity of 26,000 cu. metres; after 1908, at the Bovisa (Milan) works a new one was brought into use which holds 80,000 cu. metres and cost little less than £40,000. The firm of Krupps constructed for their own works a gasometer holding 37,000 cu. metres;

the largest at Berlin contains 80,000 cu. metres; that of Chicago 120,000 cu. metres; and the last built at New York has a cement reservoir and a capacity of 500,000 cu. metres; in London in 1888 one was built holding 230,000 cu. metres, and in 1892 another with six bells, containing 345,000 cu. metres and having a diameter at the base of 95 metres; the last built at Vienna contains 250,000 cu. metres. Naturally these gas-holders represent large amounts of capital, the cost even for capacities of 30,000 to 40,000 cu. metres being tens of thousands of pounds. Fig. 67 shows diagrammatically the arrangement of a gasworks at the middle of the nineteenth century.

PRESSURE REGULATORS FOR CONSUMERS. In order that consumers may have a uniform pressure in their pipes and obtain regular, non-oscillating flames with a normal consumption of gas, it is necessary to use pressure regulators where the principal mains leave the works, these regulating the pressure automatically even when the consumption is at its maximum or minimum. Since gas is lighter than air, the pressure is regulated more easily, and the flow facilitated, by constructing the works at the lowest point of the town. In the gas-holder the pressure is usually 15 cm. of water, whilst in the mains it is about 2 cm.

A regulator as ingenious as it is simple was devised by Clegg and is in general use at the present time (Fig. 68). In a metal cylinder, *a*, filled with water, a bell, *b*, may be raised or lowered according as the gas supplied at *f* has a greater or less pressure. The pressure in the bell may be varied by altering the size of the aperture in tube *f* by which the gas is admitted. The orifice *i* at the upper end of *f* can, indeed, be closed to a greater or less extent by a metal cone, *e*, attached by a chain to the bell, with which it rises if the pressure is excessive—thus diminishing *i* and hence the pressure in the bell—or falls if the pressure diminishes too much, more gas then entering through *i* and the normal pressure being thus re-established. This normal pressure may be fixed according to the needs of any particular time, by placing on the bell weights, *d*, calculated to give the required pressure. By means of this simple regulator the gas issues from *h* at a constant pressure and may be passed immediately into the mains.

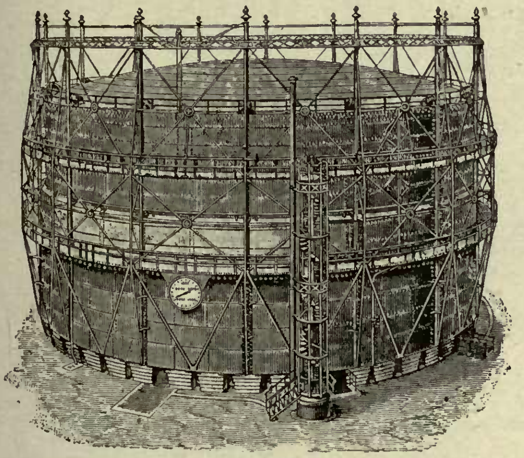
FIG. 65.

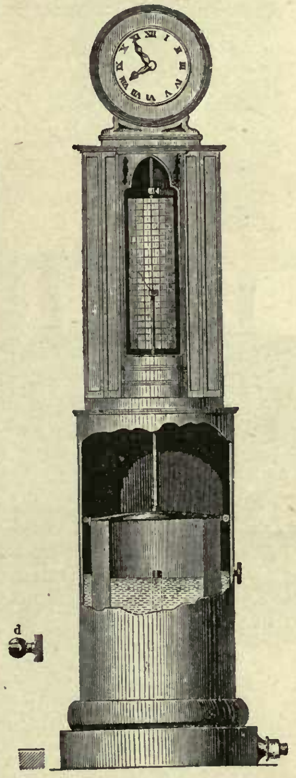

FIG. 66.

In general, however, the pressure is not the same in all the mains, but diminishes as the distance from the works increases. It is, however, not advisable to have the pressure too high, since the losses due to unavoidable leaks in the pipes are greater the higher the pressure, and the latter is usually maintained at 15 to 20 mm. of water at the points most remote from the works.[1]

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[1] Leaks in the street mains are detected by driving into the ground glass or iron tubes containing paper soaked in palladious chloride or iodic anhydride, which is darkened by the action of CO (*see* Vol. I., p. 484).

TRANSPORT OF GAS TO A DISTANCE. Attempts have been made to convey gas to great distances under 1 or even 2 atmospheres' pressure, in order that smaller pipes might be used. Under these conditions, however, increased leakage occurs,[1] while sometimes liquid and solid matter separates and obstructs the pipes. Avoidance of this inconvenience requires special purification of the gas and its subjection to intense cooling (according to Lipinsky's Ger. Pat. 257,534 of 1912, the CO is transformed into methane by the method of Sabatier and Senderens: *see* note, p. 58), the naphthalene being carefully separated. Gas produced in vertical retorts is best suited for distribution under pressure.

In order to render the distribution of the gas to considerable distances more economical, attempts have been made to employ a pressure of 1 to 1·5 atmos. on the gas, the latter being preferably from vertical retorts and as free as possible from naphthalene.

GAS-METERS. These are used to measure the gas in factories and private houses, since nowadays payment is according to the volume consumed and not according to the number of burners, as was once the custom. Dry meters have disappeared almost everywhere, general use being made of the water meters devised by Clegg and by Malam, and since improved so that they are now perfect gas-measurers. The principle on which their working is based is shown clearly by Fig. 69, representing an old form of the Malam meter. A cylindrical chest, X, half-filled with water, contains a drum rotatable about a horizontal axis and divided into four chambers, A, B, C, and D, communicating at the centre by means of the narrow slits b, and opening into the periphery at X by the slits c. The gas is led by the tube a into the central part of the drum and, in the position shown in the figure, communicates only with the slit b of the chamber D; the latter is thus slowly filled with gas (which has a slight pressure), the drum being thereby raised and water caused to escape from c. Thus the chamber D becomes filled with gas in the position occupied by C,

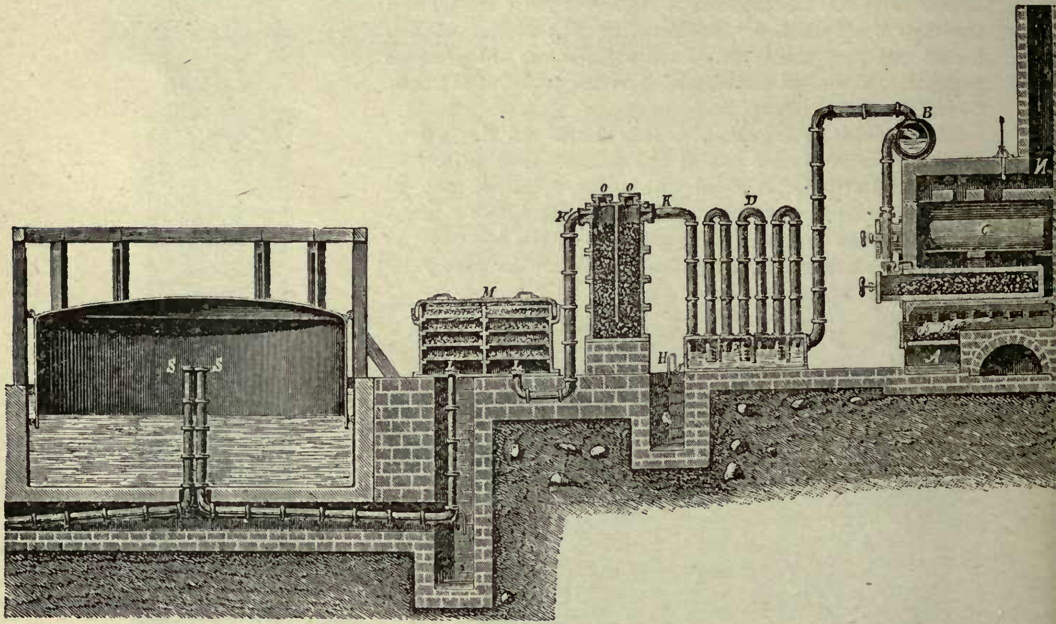

Fig. 67.

C = horizontal retorts; B = hydraulic main for separating the tar; D = tubes for cooling gas; O = washing towers (*scrubbers*); M = chambers containing Laming mixture for purifying; G = single-lift gasholder; SS = entry and exit gaspipes.

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[1] Gasworks always experience gas losses, indicated by the difference between the amounts registered by the works meters and those shown by all the meters of their customers. Such losses vary from 1·5 to 18 per cent., and are due, not solely to leaks in the pipes, but more especially to errors in the meters, to condensation of water in the pipes caused by differences of temperature, etc. In Pennsylvania these losses are only 1·9 per cent., in Virginia 18 per cent., in Bradford 4·8 per cent., in Glasgow 8·7 per cent., in Stuttgart (Germany) 1·2 per cent., and in Essen 13 per cent. Losses due to leakage may be diminished to one-tenth of their usual amount by using pipes welded autogenously every 10 metres into lengths of 60 metres.

which has allowed its gas to escape gradually, the rotation indicated by the arrow having caused it to fill with water through the corresponding slit *b*. Subsequently the gas fills the next chamber, *A*, which displaces *D*, and so on. The gas passing through this apparatus proceeds along the tube *K* to the consumer's burners. If all the taps are turned off, the drum cannot allow the gas to escape from it, and hence does not turn. The chambers have definite volumes, and if the axis of the drum is connected with a suitable magnifying apparatus the number of turns of the drum and consequently the volume of gas traversing it may be measured.

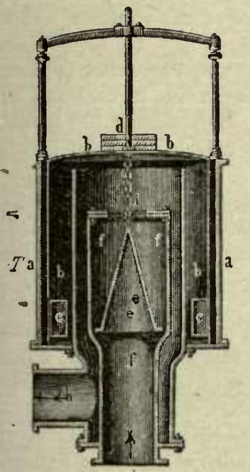

Fig. 68.

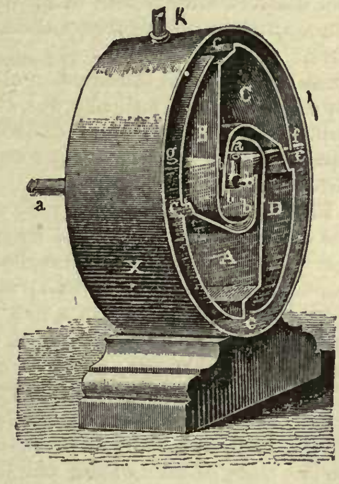

Fig. 69.

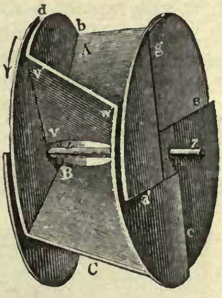

Fig. 70.

This apparatus exhibits many structural defects which cause inaccurate measurements, and are now avoided by the meter shown in Figs. 71, 72, and 73. Here the drum has transverse walls which are inclined and not parallel to the axis (Fig. 70, *V*, *W*), so that the filling with the gas or water and the discharge take place gradually and do not cause oscillation of the flame. The gas enters by the tube *l* into the division *k* (Figs. 71 and 72) and passes into *E* through the orifice *i*, regulated by a floating valve, *h*. Thence the gas goes to the ante-chamber *B* by way of the elbow-tube *n x*, opening above the level, *W*, of the water. The aperture *o* connecting the tube *x* with the ante-chamber is large enough to admit of the passage of the axis of the drum, but remains closed owing to the level of the water being above it. As the slits of the drum gradually present themselves, the gas enters successively the chamber of the drum from one side and issues at the other into the outer casing *A*, then passing through the tube *g* to the

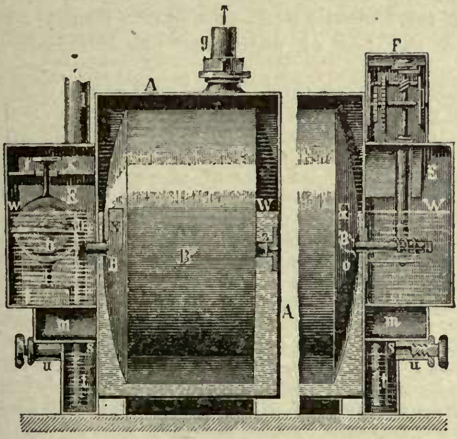

Fig. 71.

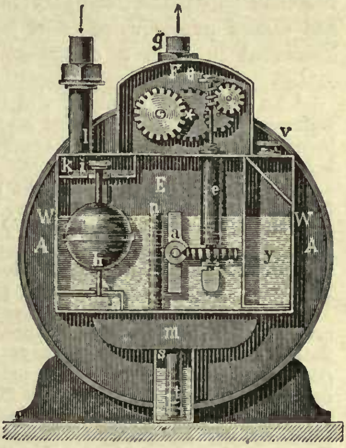

Fig. 72.

gaspipes. Water (or better, a mixture of water and glycerine, which does not freeze) is introduced by the opening *V*, the level of the liquid being fixed by the tube *n*, so that the flow of gas through the valve *i* is regulated; the excess of water is discharged by the tube *n* and passes into the reservoir *m*, thence by the tube *t* to *S*, the orifice, *u*, of which is left open while the water is being added. The axis of the rotating drum has, at one end, a continuous screw, *a* (Fig. 73), which moves a toothed wheel, *α*; the latter, by means of the axle *e*, produces rotation of a clockwork arrangement in *F*, so constructed that one wheel indicates litres and tens of litres, another cubic metres, a third tens of cubic metres, and a fourth hundreds of cubic metres.

The last few years have seen the successful introduction of the new *dry meters* (which, however, rapidly become less exact than the ordinary wet meters, when in use) and of *automatic meters*, of which Berlin alone contained 84,000 in 1905. By placing a 10-pfennig piece into one of these automatic metres, 500 litres of gas are supplied. In 1906 Berlin had, in addition, 191,000 ordinary meters.

YIELD, VALUE, AND PRICE OF GAS. These vary with the nature of the coal used and with the conditions of carbonisation. In the large gasworks of the principal European towns the yields (per ton of coal carbonised) usually vary between the following limits: coke, 63 to 76 per cent., more commonly 69 to 71 per cent. (1 hectolitre weighs 34 to 37 kilos); tar, 4 to 6 per cent.; ammonia liquors, 9·8 to 12·5 per cent. (*i. e.*, 0·8 to 1 kilo of ammonium sulphate); gas, 25 to 31 cu. metres (of sp. gr. 0·360 to 0·480). At Berlin every ton of coal yielded on the average 287·3 cu. metres in 1900, 305 in 1901, 320 in 1902, and 324·4 in 1904, in addition to 690 kilos of coke, 54 kilos of tar, and 120 kilos of ammonia liquors.

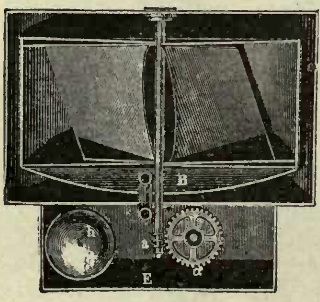

Fig. 73.

In many gasworks at the present day, instead of installing new plant, increased consumption of gas is met by mixing with *water-gas* (or *blue gas*), and as the calorific value of this is only about one-half that of coal-gas, benzene or heavy petroleum vapours are also added. Water-gas generators give a rapid production, do not form naphthalene or tar, and yield a gas costing less than half that of ordinary gas; this is, however, very rich in carbon monoxide, which has caused numerous cases of poisoning in the United States, so that the medical men instituted in 1910 a campaign to forbid the use of water-gas.[1] Nevertheless, in

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[1] To obtain a candle-power of 16 with a mixture of two-thirds of coal gas and one-third of water-gas, 40 grams of benzene must be added per cu. metre (4 grams of benzene per cu. metre increase the luminosity by 1 candle-power), the cost being about 0·5*d*. per cubic metre (with benzene at £10 per ton).

During the European War the benzene and toluene (about 25 grams of the two out of the 35 grams present per cubic metre) were extracted in all countries from coal-gas and from coke furnace gas (*see* Vol. I., p. 451) by washing the gas in towers containing circulating heavy tar oil (b.-pt. 250° to 300°), which constitutes a good solvent for these substances; the benzene and toluene are afterwards distilled off from the oil, which is used again (*see later*, Benzene). Naturally the gas loses in heating power and luminosity by this process.

Water-gas, reinforced with benzene and mineral oils, costs about 15 per cent. more than ordinary gas, but presents various advantages: without expensive plant, a production higher than the capacity of the works may be supplied; part of the coke is utilised, over-production and consequent lowering of the price being thus avoided; less consumption of coal for gas and hence less danger of rise in price of coal; less labour; rapid production even in the event of a strike. In England over 500,000,000 cu. metres were produced in 1910 and in the United States 2200 million cu. metres. Water-gas may be rendered less injurious by diminishing the proportion of CO by the processes mentioned in Vol. I., pp. 141, 484, and 486, or, as at the Lyons gasworks, by passing the gas mixed with steam over ferric oxide at 400° to 500°: $Fe_2O_3 + 4CO + H_2O = 4CO_2 + H_2 + 2Fe$, the CO_2 being then removed by washing with water. Water-gas contains 85·4 per cent. H, 9·4 per cent. CO, and 5·2 per cent. O and N, has the sp. gr. 0·18 and the calorific value 2490 Cals. per cu. metre, and is most suitable for airships (*see* note, p. 40).

Attempts have also been made to diminish the content of CO by means of the Sabatier and Senderens process (*see* p. 35), *i. e.*, by converting it into methane by the action of finely divided nickel at 250°; for this conversion to be complete the ratio between the CO and the H_2 must be 1 : 5 (water-gas actually contains about 40 per cent. of CO and 52 per cent. of H_2 by volume). The nickel catalyst is rapidly paralysed by the sulphur and by the carbon separating. These inconveniences are overcome by the Cedford process, in which the gas is compressed to 10 atmos. in presence of water, which dissolves most of the CO_2, the rest of the latter being fixed by lime.

almost all the large gasworks of different countries a mixed gas containing 15 to 20 per cent. of water-gas is made.

The cost of manufacture of coal-gas varies with the different factors affecting its production, especially with the size of the works, the prices of coal and labour and the greater or less completeness with which the secondary products (ammonia, cyanides, sulphur, tar, etc.) are utilised. In Berlin the mean cost of manufacture before the war was 0·75*d.* per cubic metre, while at Milan it is about 0·85*d.*[1] Gas varies in price in different towns from 1·15*d.* to 3·8*d.* per cubic metre (32*d.* to 100*d.* per 1000 cu. ft.); in Paris it is 1·9, in Milan 1·25, in Oneglia 2·9, in Messina 3·2, in Venice 3·5, in Catania 3·8, and in Naples 3·1*d.* per cubic metre. (In England often much cheaper.—*Translator.*)

During the war prices were in some cases trebled, and in Italy the output was largely diminished owing to scarcity of coal; in 1919 high prices still prevailed everywhere.

STATISTICS. The consumption of lighting gas (subject to tax) in Italy in 1902 was 139 million cu. metres, and exempt from taxation (for engines, etc.) 56 million cu. metres, and in 1909, 318 million cu. metres (£2,040,000), obtained from 1 million tons of coal, 51,000 tons of tar, and 710,000 tons of coke being recovered.[2]

In 1906, 16 million tons of coal were carbonised in Great Britain to procure 4300 million cu. metres of illuminating gas, and in 1909, 4760 million cu. metres were produced, besides 588 million cu. metres of carburetted water-gas.

In 1859, Germany consumed 44 million cu. metres of gas, in 1879, about 350 million, in 1889, about 500 million, in 1899, almost 1200 million (from about 3,500,000 tons of coal), in addition to 1 million tons of petroleum, corresponding with more than 2000 million cu. metres of gas. In 1905, 310 large gasworks used 4,500,000 tons of coal, of which one-fourth was imported from England, and 700 other small works carbonised a total of 1,000,000 tons; in 1910, the output of gas was 2200 million cu. metres, made in 1200 works, representing a capital of £80,000,000 (£12,000,000 for Berlin and £640,000 for Munich), the coal carbonised

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The remaining gas is cooled to the temperature of liquid air by means of a Linde machine (*see* Vol. I., p. 343), most of the CO and N_2 being thus removed in the liquid state and the sulphur compounds as solids; the residual gas contains 17 per cent. of CO, and the liquefied CO is used for gas-engines. The gas containing 17 per cent. of CO is passed into a quartz tube filled with pumice coated with finely divided nickel and heated at 280° to 300°, all the CO being thus transformed into CH_4 (if carbon is deposited on the nickel, the gas current is slackened : $C + 2H_2 = CH_4$). The final gas has the following percentage composition : CO_2, less than 1; CO, less than 0·2; CH_4, 28 to 32; H, 60 to 65; N, 6 to 7, its calorific value being 4100 to 4300 Cals. By repeated addition of CO, a gas containing 76 per cent. of CH_4 may be obtained. This Cedford gas may be added with impunity to illuminating gas.

[1] We give here an approximate industrial balance-sheet referred to one ton of coal and to the conditions employed in the Milan gasworks prior to the war :

(*a*) *Receipts :* 264 cu. metres of gas (290 actually produced, less 9 per cent. for escapes and consumption in works) at 0·13 lira gives 34·32 lire; 700 kilos of coke, 22·40 lire; 45 kilos of tar, 1·35 lire; 9 kilos of ammonium sulphate, 2·70 lire; cyanides, graphite, slag, ashes, 0·06 lira. *Total receipts,* 60·83 lire.

(*b*) *Expenditure :* 1 ton of coal, 30 lire; coke for heating the furnaces (160 kilos), 5·12 lire; purifying and Laming mixtures, 0·37 lira; sulphuric acid and expenses for ammonium sulphate, 1·44 lire; salaries and wages, 10·58 lire; taxes, 0·67 lira; fire insurance, 0·091 lira; workmen's insurance, 0·175 lira; general expenses, 1·10 lire; maintenance of works, private and public expenses, new plant, 3 lire; maintenance of meters and sundry other expenses, 0·090 lira. *Total expenditure,* 53·23 lire.

Net profit, about 7·60 lire.

[2] At Milan in 1903, 40 million cu. metres of gas were produced, in 1905 about 47 million cu. metres, in 1908 about 61 million cu. metres (7000 incandescent gas lamps being used for public lighting), in 1913, 62,433,500 cu. metres, in 1915, 65,571,660 cu. metres (3,314,200 for power purposes), and in 1916, 60,136,140 cu. metres. Paris alone consumes annually 350 million cu. metres, two-thirds by night and one-third by day (for engines, etc.), and Berlin used in 1908 about 250 million cu. metres and in 1911 more than 530 millions (in this city gas manufacture is municipalised, and the community draws an annual profit of about £350,000). From 1886 to 1904, the consumption in Brussels increased from 15 to 39 million cu. metres, that is, from 85 to 204 cu. metres per head per annum. In Budapest 300,000 cu. metres of gas per day were consumed in 1913.

The various sources of light used to supply the needs of Paris in 1889 were in the following proportions : wax, tallow, stearine, 1·6 per cent.; vegetable oils, 4·5 per cent.; petroleum, 17·7 per cent.; electricity, 18·9 per cent.; gas, 57·3 per cent. In Berlin, where the consumption of gas in 1889 was 117 million cu. metres and where 54,000 tons of petroleum were used for lighting purposes, the proportions were as follows : petroleum, 50 per cent.; gas, 47 per cent.; electricity, 3 per cent. In 1910 the consumption of gas in Berlin was 182,500,000 cu. metres, containing 32,500,000 cu. metres of water-gas obtained from 15,100 tons of coke.

amounting to about 6,300,000 tons. In 1913, the production of gas in Germany reached 3160 million cu. metres, 10 million tons of coal being used [1] and by-products to the value of £4,800,000 obtained.

In the United States 600 million cu. metres of gas were produced in 1900, and more than 870 million in gasworks in 1905, besides 275 million in coke works and 2200 million of water-gas.

In 1909, there were in the United States 1296 gasworks (1019 in 1904) with a capital of £180,000,000; the output of gas and by-products was valued at £33,600,000, and the numbers of workpeople and officials employed, 37,200 and 13,500 respectively. The gas produced amounted to 4200 million cu. metres (including water-gas, which constituted 53 per cent. of the total).

In Japan the lighting gas industry was started only in 1901, 44 million cu. metres being produced in 1907.

In Switzerland, 500,000 tons of coal are carbonised annually for making coke and gas, 30,000 tons of tar, 1500 of naphthalene, 450 of benzene and toluene, and 75 of phenol also being obtained.

The manufacture and nature of air-gas, producer gas, Riché gas, water-gas, etc., are described in Vol. I., pp. 486 *et seq.*

PHYSICAL AND CHEMICAL TESTING OF ILLUMINATING GAS. As regards the determination of CO, CO_2, N, and O, Orsat's apparatus (*see* Vol. I., p. 463) gives good results. The estimation of hydrogen is effected with the ordinary Hempel burette or simply by determining the diminution in volume of the gas after passing it through a capillary tube containing palladinised asbestos heated at about 100° (*see* Vol. I., p. 135). Then comes the determination of unsaturated and aromatic hydrocarbons, which are all absorbed by fuming sulphuric acid, the gas being measured before and after the absorption in the Hempel burette (the gas being washed with potash after the absorption). The methane is estimated by exploding the gas remaining in the burette with a known volume (in excess) of oxygen by means of an electric spark, 2 vols. of the gaseous mixture (gas + oxygen) disappearing for every 1 vol. of methane, according to the equation:

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{condenses}}{2H_2O}.$$

To estimate the *ammonia* in the purified gas, 200 litres of it are passed through 10 c.c. of N/10 hydrochloric acid solution, the excess of which is subsequently determined by titration.

The determination of the total *sulphur compounds* may be effected simply by the method given by F. Fischer.[2]

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[1] For the production of gas in Berlin 352,000 tons of German coal and 397,000 tons of English coal were used in 1907; at the English ports the coal cost 8*s.* 1½*d.* per ton in 1904 and 11*s.* 4½*d.* in 1909. The cost of transport from the English mines to Berlin amounted to 7*s.* 3½*d.* per ton, whilst from the German mines at Ruhr to Berlin it exceeded 8*s.* 11*d.* At the gasworks in Berlin the English coal cost 16*s.* per ton, and the German (from Silesia) 20*s.* per ton.

In 1880 only one-half of the gasworks were municipalised, and in 1909 two-thirds, the profit amounting to 8 to 13 per cent. on the capital.

In Germany in 1910 35,000 gas-engines generated 175,000 h.p. (in 1898 there were 22,000 engines), 50 per cent. of the total output of gas being used for power and heating purposes (in 1898, 33 per cent.). It is found profitable to erect a gasworks in Germany in centres containing over 3000 inhabitants. In 1911 the receipts of the German Government on account of taxes on illumination were as follows: £108,000 for carbon-filament electric lamps; £292,000 for metal filament (and Nernst) lamps; £1600 for mercury vapour lamps (*see* Vol. I., p. 687); £216,000 for incandescent gas lamps; £90,000 for arc lamps with pure carbons; £64,000 for arc lamps with special carbons containing admixed luminous substances. In Germany between April 1, 1911, and March 31, 1912, there were made: 24,791,200 carbon filament lamps (1,585,700 imported), 47,212,000 metallic filament lamps (1,450,000 imported), 130,671 Nernst lamps (output diminishing), 12,050 mercury vapour lamps (1500 imported), 126,000,000 Auer mantles (35,000 imported), 8,104,000 kilos of pure carbons for arc lamps, and 2,637,000 kilos of carbons with various additions.

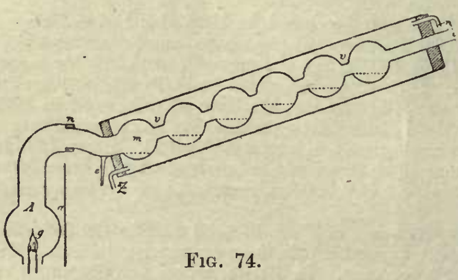

FIG. 74.

[2] About 50 litres of the gas (measured by a good meter) are burned in a small bunsen burner, *g* (Fig. 74), in the drawn-out bulb, *A*, of a bulb-condenser arranged as shown. All the sulphur of the sulphur compounds burns, forming sulphurous and sulphuric acids with the water from

For the *complete analysis* of gas, *see* Treadwell's "Quantitative Analysis." The *calorific power* may be determined fairly rapidly with the Junker calorimeter.[1]

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the combustion of the gas, this condensing in the bulbs of the condenser and being collected at the bottom in a beaker by means of the tube *e*. The combustion is regulated so that gas containing 4 to 6 per cent. of oxygen escapes at *o*. Water enters the condenser at *z* and leaves at *n*. At the end of the operation, the bulbs are rinsed out with water and the sulphurous acid in the liquid oxidised by means of pure, neutral hydrogen peroxide solution; the sulphuric acid is then titrated with N/10 sodium hydroxide solution. If the sulphuric acid is estimated gravimetrically with barium chloride, the oxidation of the sulphurous acid must be effected with hydrogen peroxide free from sulphates. The quantity of sulphuric acid found gives the total sulphur-content of the gas. A well-purified gas contains less than 0·5 gram of sulphur per cubic metre.

The *hydrogen sulphide* is estimated separately by passing a known volume of the gas through ammoniacal silver nitrate solution, which is afterwards acidified with a little nitric acid, the silver sulphide being filtered off, washed, dried at 100°, and weighed.

The *naphthalene* is determined, especially in the crude gas (which contains 8 to 10 grams per cubic metre), by passing a certain volume of the gas through saturated picric acid solution and filtering off the insoluble naphthalene picrate, which is then boiled with water in a current of air. In this way it decomposes into picric acid and naphthalene, the latter being passed into another standard picric acid solution, the excess of picric acid being determined with standard potassium iodide and iodate solution: $KIO_3 + 5KI + 6C_6H_2(NO_2)_3OH = 6C_6H_2(NO_2)_3OK + 3H_2O + 6I$; the iodine liberated is titrated with thiosulphate solution.

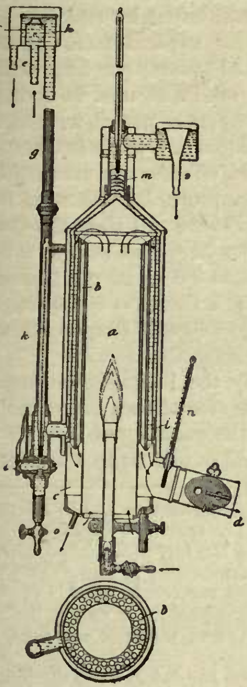

FIG. 75.

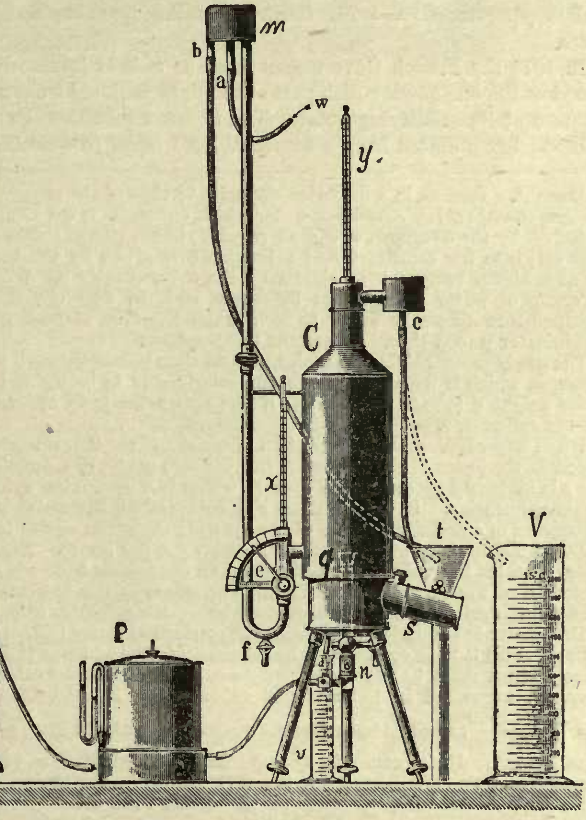

FIG. 76.

[1] This consists (Fig. 76; section in Fig. 75) of a metal cylinder, *C* (the letters refer in all cases to Fig. 76), which is mounted on three feet, and inside which a known volume of the gas is burned by means of the bunsen burner, *n*. The hot products of combustion pass several times up and down the calorimeter and issue at the outlet *S*, which is furnished with a valve and also regulates the

The *specific gravity* sometimes serves to test the constancy in composition of gas or to compare two different gases; it also gives a rough idea of illuminating power, since the specific gravities of the more highly light-giving hydrocarbons—acetylene (0·920), ethylene (0·976), propylene (1·490), and benzene (2·780)—are higher than those of the non-luminous components—hydrogen (0·0695), methane (0·559), etc. The specific gravity may be determined rapidly and exactly with the Bunsen *effusiometer* (*see* Vol. I., p. 40).

ILLUMINATING POWER. There is no absolute measure of the power of different sources of light, but these may be compared when a conventional unit has been chosen.

This *standard of light* has been differently chosen in different countries and has been continually modified. Thus in England spermaceti candles are used of such size that six weigh 1 lb., while, when burned, they lose 7·78 grams (120 grains) per hour with a flame 45 mm. in height. In Germany in 1872 a paraffin wax candle 20 mm. in diameter was employed, the wick having 24 threads and weighing 0·668 gram per metre and the flame being 50 mm. high; six of these candles weighed 1 lb. Use is now made in Germany of the more rational Hefner-Alteneck lamp, fed with a liquid of constant composition, namely, amyl acetate, the compact wick, 8 mm. in diameter, protruding 25 mm. from the metallic sheath holding it; the flame is 40 mm. high. In France and Italy the Carcel lamp is used, this consuming 42 grams of purified colza oil per hour and having a wick which is 23·5 mm. in diameter, is formed of 75 threads, and weighs 3·6 grams per 10 cm.

The relative values of these different units are as follows: 1 Carcel = 9·600 English candles (spermaceti) = 8·768 German candles (paraffin wax) = 10·526 Hefner-Alteneck flames.

In 1914 the French Government fixed as unit of luminosity the *Violle decimal candle*, defined as the one-twenty-fifth part of the light radiated from an area of 1 sq. cm. of molten platinum at its solidifying point. The *lumen* would then be the quantity of light or the luminous flux radiated from a source of light equal to a decimal candle on to a surface of

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air-draught. Passing in a direction opposite to that of the gases of combustion and in alternate adjacent chambers is a current of water which enters by *w* the small reservoir *m*, the excess being carried off by the overflow, *b*, while a regular stream passes through the tap *e* (furnished with an indicator) into the calorimeter at a temperature given by the thermometer *x*, and flows away at *c* at a higher temperature, shown by the thermometer *y*. When the combustion is started, the entry of water is regulated by means of *e*, so that the thermometers *x* and *y* indicate a temperature difference of 10° to 20°; when the flow of both gas and water is constant, the thermometer *y* soon shows a constant temperature.

The gas is measured by the meter, *G*, and then passes through the regulator, *P*, to the bunsen burner, *n*, which is withdrawn from the calorimeter to be lighted and is then pushed in again to the height *q* (about 6 in. up). If the apparatus is in order, no water should fall from *d* into the cylinder, *v*.

When water is discharging from *b* and from *c*, and the thermometric reading remains stationary, as soon as the index of the meter reaches the zero mark, or a definite number of litres, the rubber tube *c* is instantly placed from *t* into *V*, which is a graduated cylinder placed quite close to the discharge-funnel, *t*. In the cylinder *V* is collected all the water which is discharged during the combustion of a definite volume of gas (in the proportion of 100 to 200 litres of illuminating gas or 400 to 800 litres of suction gas or Dowson gas per hour). Exactly at the moment when the meter indicates the volume of gas fixed upon, the rubber tube *c* is removed from *V* to *t*. During the course of the experiment the small variations in the indications of the thermometer *y* are noted at intervals, the mean temperature being subsequently calculated.

The graduated cylinder, *v*, contains the condensed water (*a* c.c.) formed during the combustion of the gas, and this, in condensing, has given up to the water of the calorimeter a certain quantity of heat, which must be subtracted before calculating the *net calorific power*. The *gross calorific power*, *U*, expressed in Calories per cubic metre, is calculated by means of the formula: $U = \frac{A \,.\, T \,.\, 1000}{Q}$, where *A* indicates the quantity of water in litres collected in *V*, and *Q* the volume of gas burned. If, for example, $Q = 3$ litres, $A = 0{\cdot}900$, $T = 18°$ (that is, 26·77°, the mean of six readings of the thermometer *y*, less 8·77° shown by the thermometer *x* to be the temperature of the water entering at *e*), we have $U = \frac{0{\cdot}900 \,.\, 18 \,.\, 100}{3} = 5400$ Calories per cubic metre of gas. In general the calorific value is now referred to 1 cu. metre of gas calculated at 0° and 760 mm. pressure. In cases where the gas is used in engines or other apparatus from which the products of combustion issue at a temperature above 65°, the water-vapour does not condense, and the *gross calorific power* (*U*) must be diminished by the heat due to the condensation of the water-vapour produced by the combustion of the gas in the calorimeter. From *U* must hence be subtracted a value obtained by multiplying by 60 the number of c.c. of water condensing during the combustion of *Q* litres of gas. This *net calorific power*, U^1, is, for illuminating gas, usually 10 per cent. lower than the *gross calorific power*, *U*.

The calorific values of different industrial gases are given in Vol. I., p. 489.

1 sq. metre of a sphere of 1 metre radius; the *lux* would be the unit of illumination, that is, the illumination of an area of 1 sq. metre produced by 1 lumen.

The luminous unit being fixed, different sources of light and their illuminating powers may be compared by means of *photometers.*[1]

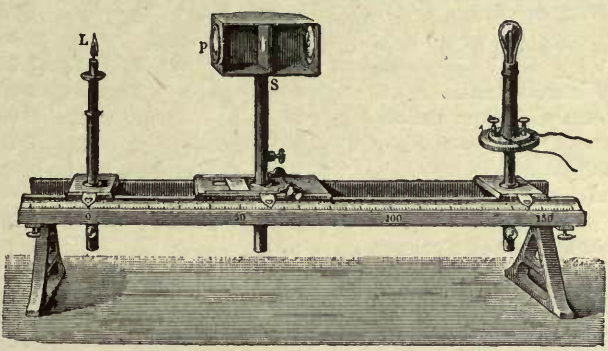

Fig. 77.

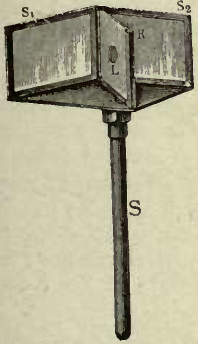

Fig. 78.

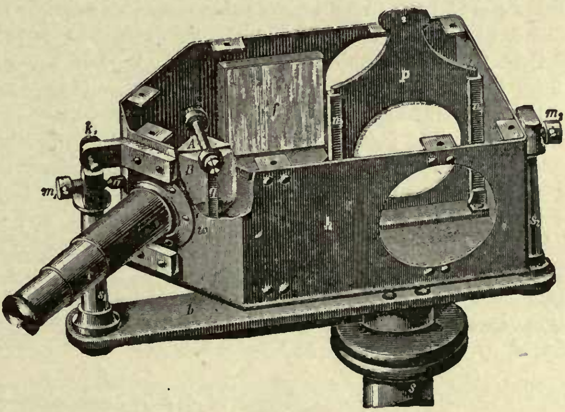

Fig. 79.

[1] Of these, the one most largely used is that of Bunsen, which is based on the principle that the intensity of light produced on a definite surface by a source of light is inversely proportional to the square of the distance. If the distance between the source of light and the surface illuminated is trebled, the intensity of the illumination is diminished to one-ninth of its previous value. The luminosities of two flames, I and I_1, which illuminate equally a given screen and are at the respective distances L and L_1 from it, are directly proportional to the squares of these distances: $I : I_1 = L^2 : L_1^2$, and if I_1 is the unit of measurement, the intensity of the other source of light will be: $I = \frac{L^2}{L_1^2}$. The Bunsen photometer (Fig. 77) consists of a horizontal iron photometer bench 3 metres long and divided decimally (into half-centimetres or millimetres); at one end is placed the comparison electric or candle lamp or the Carcel lamp, the consumption of oil in which is regulated by a small pump actuated by a clockwork mechanism, weighing on a balance the consumption in a given time (indicated by a bell)—this corresponding with 42 grams of oil per hour. A screen of paper may be moved backwards and forwards along the bench and normally to it, the middle of the screen being rendered translucent by means of a grease-spot (spermaceti); at the other end of the bench is placed the light to be examined. When the screen is equally illuminated on its two faces, the grease-spot is no longer perceptible. The intensities of the two sources of light are then proportional to the squares of their distances from the screen.

The measurement is made in a dark room and, in order to render more evident the disappearance of the spot on the two surfaces, the screen is placed between two mirrors arranged at an angle (Fig. 78). An improvement on the Bunsen photometer has been made by Lummer and Brodhun, who substitute for the screen with the grease-spot a closed box, h (Fig. 79), in which are two opposite circular apertures, these illuminating the two faces of a white screen, f, by means of light from the standard lamp, and that to be tested, placed at the two extreme ends of the photometer bench. By means of a system of prisms, A B, the two faces of the white screen reflect the light on to two concentric zones of the field of the eye-piece, r. When the two faces of the screen are equally illuminated, the two zones of the field also appear uniformly lighted.

COMPARISON BETWEEN VARIOUS SOURCES OF LIGHT. To produce the luminous intensity of a Hefner candle-hour (HK), the following quantities of lighting materials must be consumed:

Candles	Stearine, first quality	7·87 grams
	„ third „	9·58 „
	Paraffin wax	6·27 „
	Two parts of paraffin wax and one of stearine	6·93 „
Lamps	Carcel: colza oil	3·99 „
	Petroleum, flat wick	2·76 „
	„ round wick	2·80 „ 3·60 „
	Spirit: incandescent	1·90 „
	Petroleum with Auer mantle	0·50 „
Acetylene		0·6 litres
Gas burners	Fish-tail	19·0 „
	Argand	10 „
	Auer	1·60 „
	Millenium (gas under pressure)	0·75 „
	Auer with inverted flame	0·70 „
Electric lamps	Arc lamp of small power	1·20 volt-amps.
	„ „ high „	0·25 „
	Incandescent Edison	3·70 „
	Metallic filament (osmium, tantalum)	1·90 „
	Mercury vapour	0·50 „

It is easy to calculate the cost from the prices of the various methods of lighting, these varying from town to town and from country to country. In 1896 Lüpke calculated the following numbers of normal candle-hours to be obtainable for one mark (one shilling), the calculation being valid only for that period and for Germany: wax, 33; stearine, 77; colza oil, 150; electric lamp with incandescent carbon filament, 150; fish-tail gas-jet, 625; acetylene and air with an edged burner, 716; oil-gas, 1660; water-gas with benzene, 1666; electric arc lamp, 2232; Auer gas lamp, 2300; Auer water-gas lamp, 4350.

From gas at 1·9*d.* (0·2 lira) per cubic metre, as a source of heat, 1000 Cals. are obtained for 0·38*d.* (0·04 lira), whilst, using electric current at 3·07*d.* (0·32 lira) per kilowatt-hour, 1000 Cals. would cost about 3·65*d.* (0·38 lira). For power purposes, the electric current [at 2·4*d.* (0·25 lira) per kilowatt-hour] costs more than double as much as gas [at 1·73*d.* (0·18 lira) per cubic metre].

During the past few years a considerable advance has been made by the use of incandescent electric lamps with metallic filaments (tantalum, tungsten, osmium, etc.), which reduce the consumption of electrical energy by one-half, but at the same time gas lamps have been improved by the use of high-pressure gas, and those with inverted flames are still decidedly more economical than metallic filament electric lamps. From the hygienic point of view the disadvantages of gas lighting have been exaggerated, as it has not been realised that the use of gas causes circulation and renewal of the air, and that the production of water-vapour and carbon dioxide are negligible compared with the similar effects produced by the respiration of human beings.

OIL-GAS

In cases where the installation of a plant for the carbonisation of coal would be inexpedient, owing to the small consumption of illuminating gas, it may be convenient to prepare oil-gas by dropping into a red-hot retort (*see later*, "Cracking" Process in the Petroleum Industry) fatty residues, lignite, tar oils, resins, and medium petroleum oils (blown oil, *see* Petroleum). This destruction by heat (at 745° to 790°) produces a gas which consists mainly of C_2H_4 and H_2, and when compressed at 10 to 12 atmos., to separate part of the heavy, liquid hydrocarbons (with slight loss of calorific value), and enriched with 25 per cent. of acetylene, is used for the illumination of railway carriages. Oil-gas may also be prepared easily and abundantly by dropping oil into gas-producers containing red-hot coke.

Davis (1910) avoids the formation of tar by pulverising the oil in the retort by means of air instead of steam. In this way a gas is obtained having the following percentage composition: CO_2, 2; heavy hydrocarbons, 26; CO, 1·5; CH_4, 35; H_2, 5·5; and N, 30. Injection of oil-gas (two-thirds) and water-gas (one-third) into a coke gas-producer yields a gas containing 46·5 per cent. of H_2, 31·3 of CH_4, 7 of N_2, 11·6 of heavy hydrocarbons, and 2·8 of CO, its calorific value being 5490 Cals.

As early as 1815 public lighting with oil-gas was attempted (Liverpool used it for some years), but it was only after 1860–1870 that this industry assumed importance. From 100 kilos of lignite paraffin oil are obtained 60 cu. metres of gas, and with a consumption of 35 litres of the gas per hour, 7·5 normal candles (German) are obtained; its illuminating power is four times as great as that of ordinary lighting gas. One kilo of medium petroleum oil gives 600 litres of gas, 300 to 400 grams of tar, and 40 to 60 grams of coke. If a greater yield of the gas is obtained, it loses in illuminating power. The purification of oil-gas is carried out in practically the same way as that of coal-gas. Mineral oil for gas and for engines is produced in large quantities in Galicia, where it is sold for less than 19·5*d.* per cwt. (4 lire per quintal); Germany alone imported 30,000 tons of it in 1909.

PETROLEUM INDUSTRY

Crude petroleum also goes under the name of *mineral oil* or *naphtha*, and is a more or less dark liquid (according to its origin) with a peculiar, pronounced odour. It is found in various parts of the earth in the strata of the tertiary epoch and also of preceding epochs. The principal centres of production are Baku (Russia) and the United States.[1]

[1] **History of the Petroleum Industry.** The use of petroleum and of tar goes back to the earliest historical times (the Biblical legend relates that Noah rendered his ark impermeable by means of tar, and in the construction of the Tower of Babel a mortar was used prepared with naphtha !(?)). Certain races then employed naphtha as a fuel, and the Egyptians made use of it in the preparation of mummies.

In small quantities petroleum is found in nearly all countries, but 95 per cent. of the total production is given by North America and Russia. Two centuries before petroleum was used in America that from Parma in the Apennines was used for lighting, *e. g.*, at Genoa, Parma, etc. The most important petroleum wells now in Italy are in the Province of Piacenza (at Fiorenzuola d'Arda) and at Salsomaggiore, Borgo S. Donnino, and Montechino; less important deposits are found also in Calabria. At Velleia the industry has been worked for many years by a French company, many wells 200 to 450 metres deep having been sunk along the right bank of the Chero; this company was absorbed by an Italian syndicate in 1907.

In Austria the region richest in petroleum is Galicia. In 1895, when a well 300 metres deep was bored, a fountain was formed which, in thirty-six hours, yielded 5000 barrels of petroleum (1 barrel = 42 gallons = 159 litres = 145 kilos). Still more important wells in other countries are mentioned on p. 74.

In Russia the most important sources of petroleum are found in the province of Baku (99 per cent. of the whole production is obtained from an area of 6 sq. kilos), and partly at Grosny, to the north. From the most remote times, before Christ, *sacred fires*, fed by petroleum and by the inflammable gases liberated from it, have been kept burning uninterruptedly in the temples (down to 1880). During his voyage in the thirteenth century Marco Polo visited these marvellous springs of "*oil not good to use with food but good to burn and also used to anoint camels that have the mange.*"

In 1820 the Baku petroleum wells were declared the property of the Russian State, and the Government made concessions to contractors, who worked them in a primitive manner until 1872. In 1873, the most important wells and petroleum-bearing lands were put up for auction by the Government, who levied a tax on the petroleum extracted. This condition of affairs was less favourable than that holding in the American industry, so that in 1877 the tax was repealed and the Russian petroleum industry, passing into the hands of great capitalists (Nobel, Rothschild, etc.), underwent extraordinary development and often competes advantageously with that of America.

The first plant installed by Baron Thormann for the distillation of petroleum was constructed at Baku in 1858 according to suggestions and plans furnished by Liebig, carried out by one of his assistants (Moldenhauer), and improved by Eichler. The first wells bored on the American system date from 1869. Before 1870, the production was only 250,000 poods (1 *pood* = 16·38 kilos), but in 1872 it reached 1,500,000 poods, and then grew with astounding rapidity (*see later*, Statistics).

There are also important petroleum deposits in Japan, but the production is still limited:

In some places it overflows at the surface of the earth through porous rocks or clefts; in others it is found accumulated under pressure in large cavities or pockets, since, when it is reached by borings or wells, powerful jets rise above the surface of the earth often to the height of 100 metres, thus forming fountains of petroleum which last from a few weeks up to seven or eight months, and throw up also large quantities of inflammable gases and sand.

Some petroleum deposits have been gradually evaporated and oxidised

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in 1874 it amounted to 126,150 kwan (1 *kwan* = 3·78 kilos), in 1884 to 1,400,000 kwan, and in 1903 to about 126,000 tons.

During recent times important sources of petroleum have also been discovered in Canada.

In Great Britain, Young commenced in 1848 the industrial treatment of a species of petroleum discovered in a coal-mine at Alfreton; this was subjected to distillation to obtain lamp oil, lubricating oil, and a small proportion of paraffin wax, from which candles were made. Subsequently he distilled bituminous shale (*see later*), the oils obtained being refined by means of sulphuric acid and soda. In 1859 refining of petroleum by the Young system was started in America.

The greatest impulse to the petroleum industry has come from the United States, where important deposits of petroleum have been found, first in the State of Pennsylvania (in a strip of land about 100 kilometres long the production of petroleum increased from 3180 hectolitres in 1859 to 16,000,000 hectolitres in 1874, the price per barrel falling during the same period from 100 lire, or £4, to 6·5 lire, or 5*s*. 2½*d*.; these deposits are now apparently becoming exhausted), and then in Virginia, Ohio, Indiana, California, Louisiana, and Texas. At the present time the most important sources of petroleum in the United States are in the Washington district and in California.

The first studies on petroleum in America were made by Silliman in 1854, by fractional distillation, and these were followed by unsuccessful industrial efforts caused by the low production of the wells utilised and by many commercial difficulties, which were overcome by L. Drake in 1859 by the use of artesian wells.

The first petroleum well in America was obtained by pure chance; at Titusville in Pennsylvania a well was being sunk for drinking water, and when a depth of 22 metres was reached, a continuous jet of petroleum appeared, yielding 4000 litres of naphtha per day.

Just as America was taken with the "gold-fever" after the discovery of gold in California, so the United States caught the petroleum fever. Pennsylvania was invaded by adventurers, and borings were made wherever the geological formation of the earth admitted of it; all had faith in the goddess Fortune, who, as always, favoured some and drove others to ruin and despair. In 1861 the number of *derricks* (used for boring) exceeded 2000. The work was carried out hastily and without thought, usually empirically, the idea being to succeed first. Much petroleum was lost, and much was burnt, causing immense losses and ruin to numerous firms.

Great capitalist companies were then formed, and these studied calmly and rationally the technical and commercial problem, and very soon created an enormous industry, which rapidly brought petroleum into common use all over the world. Ships and railways and then iron pipes tens and hundreds of kilometres in length served to transport the petroleum rapidly, continuously, and economically from the wells to the refineries, and from these to the seaports, where it was shipped to the merchants.

In America to-day petroleum is monopolised by huge "trusts," especially the Vacuum Oil Company and the Standard Oil Company of New Jersey, to which are affiliated seventy companies with a total capital of £18,000,000 and employing 60,000 workmen and monopolising about 60 per cent. of American petroleum. The Standard Oil Company, founded in 1872, paid in dividends from 1882 to 1892 a total of £94,400,000, and from 1894 to 1903 paid to its shareholders dividends of 33 to 48 per cent.! In 1906 President Roosevelt, under pressure of public opinion, waged war against this colossal trust by rupturing the connection between the steel ring and the interests bound up with it and making them liable to a fine of over £6,000,000. In consequence of this commercial war of 1906 the Standard Oil Company lost £25,000,000, of which £12,900,000 fell on Rockefeller, the well-known millionaire president of the company. The sentence was then annulled on appeal, but the result was that the company fought its competitors by lowering prices [petroleum that previously cost 30 centesimi (2·9*d*.) per litre has been lowered in price during the last few years to 15 centesimi (1·45*d*.)], and in 1908 made a net profit of £16,000,000, and proposed raising its capital to £100,000,000. This explains how Rockefeller has been able, without any great sacrifice, to make benefactions of so many millions during the past few years, especially for the extension of university study in America. The sentence of the Supreme Court of Washington (March 15, 1911) gave judgment against the Standard Oil Company, for contravention of the law against trusts, and ordered dissolution of this powerful company within six months.

In 1912 the Standard Oil Company was indeed split up into numerous branches which, however, acquire most of the crude American petroleum and refine it in numerous works. The most important of these is the Bayonne refinery, New Jersey, which distils daily 40,000 barrels of crude petroleum to obtain benzine, lamp oil, intermediate and heavy oils, paraffin wax, etc.

during the lapse of ages, leaving a black deposit of *mineral tar*, *asphalte*, or *bitumen* (*see* section on Paraffin Wax).

ORIGIN OF PETROLEUM. Various hypotheses have been put forward to explain the origin of petroleum, and even to-day opinions are divided, probably owing to the fact that petroleum has not one single origin, since, in different parts of the earth's crust, it has different qualities and compositions (*see below*).

(1) *Hypothesis of Inorganic Origin.* A. v. Humboldt supposed petroleum to have originated from inorganic gaseous products under the influence of volcanic forces, and in 1866 Berthelot advanced the hypothesis that, by the action of carbon dioxide on alkali metals inside the earth's crust, acetylides would be formed which with hydrogen would give acetylene derivatives, these then undergoing various condensations to form petroleum and tar. Byasson in 1871 explained the formation of the hydrocarbons of petroleum as due to the action of H_2S, CO_2, and water-vapour on layers of red-hot iron, this action being produced by the infiltration of sea-water, through clefts at the bottom of the ocean, in such a way that, together with calcareous matter, it was brought into contact with deposits of heated iron or iron sulphide. Mendeléev (1877) regarded the hydrocarbons of petroleum as originating in the igneous strata of the earth's crust by the action of aqueous infiltrations on pre-existing deposits of carbide of iron or other metallic carbides. Hahn (1864) and Cloez (1874–1879) obtained support for Mendeléev's hypothesis by showing experimentally that saturated hydrocarbons and a few olefines (which polymerise under the action of pressure and heat) are formed when cast-iron or spiegeleisen (substances which contain carbide of iron) is dissolved in dilute acid. In 1891 Ross brought forward again and modified Byasson's hypothesis; he assumed that volcanic gases, especially H_2S and SO_2, in contact with heated chalky rocks, would form gypsum, with separation of sulphur and production of saturated and unsaturated hydrocarbons (this would give also an explanation of the origin of sulphur, yet in Sicily, where sulphur abounds, no petroleum is found !).

These various hypotheses on the inorganic origin of petroleum assume the formation of the latter in igneous primitive (archaic) geological strata, where the presence of organic compounds is excluded, the petroleum then finding its way to the higher layers of the earth's crust by seismic convulsions. It is, however, precisely these older archaic strata, deprived of water and of organic substances, which give no trace of petroleum. On the other hand, if the petroleum were formed in very hot strata, it should issue from the borings at a moderately high temperature, and there should have been separation of the light petroleum (more volatile) and the heavy into distinct layers. This is not actually the case.

However, during recent years this hypothesis has again come into favour, owing to the interesting work of Moissan (1894–1896) on the formation of saturated hydrocarbons by the action of water on aluminium carbide (*see* p. 35), and that of Sabatier and Senderens (1896–1902), who showed experimentally that, in presence of catalytic nickel (obtained by reduction of the oxide with hydrogen at 300°), hydrogen and unsaturated hydrocarbons (ethylene, acetylene, etc.) give rise to saturated hydrocarbons such as occur in petroleum (p. 35). Even these syntheses, however, do not yield very high and solid hydrocarbons like those present in crude petroleum, although recently (1908–1909) A. Brun, Stieger, and Becker showed that hydrocarbons similar to paraffin wax are formed by the interaction in the hot of iron carbide and ammonium chloride, even in absence of water.

(2) *Hypothesis of the Vegetable Origin of Petroleum.* This was enunciated at intervals by Binney (by distillation of peat), by Kobell (by distillation of coal), and by Bischof, who considered petroleum to be formed by the action of sea-water on cellulose and on coal included in the geological strata of the earth's crust. This hypothesis of the vegetable origin was later supported or attacked by various writers, and to the fact that, in general, carboniferous strata do not contain petroleum, is opposed the discovery of small deposits of petroleum in the coal-seams near Wombridge and of certain petroliferous substances in some Japanese coals; Höfer showed, however, in the first case, that the neighbourhood of bituminous schists, rich in the remains of fishes, could not be excluded, and, if it is desired to explain the formation of petroleum from marine vegetable organisms, it is not possible to conceive of a sufficient quantity of these to give rise to the immense amounts of petroleum now discovered. Further, other more recent geological investigations would

exclude the vegetable origin of petroleum, although the most recent chemical work tends to render such origin highly probable. It is, indeed, found that petroleum rotates the plane of polarisation of light to the right (*see later*), as do most optically active vegetable substances, whilst substances of animal origin rotate it preferably to the left. Engler, however, states that this observation is not very conclusive, since these active substances may be due to the condensation of unsaturated products originating in the decomposition of the prime materials (animals or possibly vegetables). Krämer and Potonié (1906–1907) point out that all petroleums (also certain lignites and ozokerite) contain *algæ wax*, from which, by various reactions and decompositions, it is easy to pass to substances like petroleum; and simple substances, by polymerisation (by heat and pressure), form more complex tarry substances, etc.; the presence of wax demonstrates that petroleum is formed not in the hot by distillation, but rather in the cold and at high pressures. The prime material of petroleum would hence probably be the enormous formation of *algæ* which have been produced at all epochs and are to-day accumulating in marshy places. These, during thousands of centuries and under the action of pressure and heat, could undergo the same transformations and putrefactions (mixed sometimes with animal remains), leaving the wax for the formation of petroleum; so that petroleum would be formed in all epochs and is perhaps being formed now! The varying composition of petroleum would be due, according to Krämer, to filtration through various geological strata, which would have removed greater or less quantities of bituminous products so as to produce pale, light petroleums like those of Velleia and Montechino. Hence the greater or less content of tarry substances cannot serve as an indication of the epoch of formation of a petroleum, since part of these substances may have been lost during the geological filtrations.

(3) *Hypothesis of the Animal Origin of Petroleum.* This was enunciated and vigorously upheld by Höfer, and supported and supplemented by Ochsenius (1892), Zaloziecki (1892), Veith, Dieckhoff (1893), Aisinmann (1894), Heusler (1896), Holde (1897), Aschan (1902), and Zuber (1897, who supported only the organic origin), and more especially and most exhaustively by Engler (1888–1912).

This hypothesis supposes that great layers of various fishes and molluscs, formed on the ocean-bed during past geological epochs, gradually underwent decomposition, first losing the nitrogenous components (albuminoids) as gaseous or soluble compounds, the remaining fats being slowly transformed partially into bituminous substances. These, together with the residual fats, under the action of great pressure and heat (developed, in part, by these decompositions) would yield glycerol, which would generate acroleïn and then aromatic hydrocarbons, while the remaining fatty acids (by the action of hydrogen formed in all these decompositions) would give rise to the various saturated hydrocarbons constituting petroleum, CO_2 being liberated.

The animal origin hypothesis is also supported by the observation of Fraas, that petroleum issues from the coralliferous banks of the Red Sea, and by the odour of petroleum exhibited by certain phosphorites which are undoubtedly of animal origin.

The objection has been raised that, if petroleum were of animal origin, it should contain nitrogenous compounds. Although this is not necessary, yet the presence of nitrogen products (ammonia and pyridine bases, free nitrogen and ammonium carbonate) has been shown in petroleum and in gases emanating from the earth. Texas petroleum contains up to 1 per cent. of nitrogen.

Engler showed experimentally that, under certain conditions, animal fats may be transformed into olefines or analogous products in the laboratory (by distilling fish-oil under 4 to 10 atmos. pressure). In 1909, Engler, Routala, Aschan, and others effected the laboratory production of *naphthenes*, paraffins, and heavy mineral oils, by heating amylene and hexylene under pressure and in presence or absence of aluminium chloride as catalyst.

Many facts support the view that the petroleum of the geological strata studied has been formed at a low temperature and by slow but continuous reactions lasting for thousands of years.

To the doubt that may be raised as to the enormous quantity of animal remains necessary to explain the large amounts of petroleum being raised at the present time, it may be answered that if the annual catch of herrings on the coasts of the northern seas and that of sardines by French fishermen were to accumulate on the ocean-bed for 2000 years, it would be quite sufficient to explain the petroleum production of Russia.[1]

It would, however, be necessary, for the preservation of this enormous cemetery of fish, that the corpses should not be eaten by other larger fish; the conditions must then be such that fish approaching the cemetery are killed. This is highly probable, as the existence of such conditions at the bottom of the Black Sea has recently been proved. In fact, below a certain depth, there is so much dissolved hydrogen sulphide that any animal is instantly poisoned there, its body going to swell the vast numbers that have preceded it at the bottom.

With these proofs is connected the most recent and most rational interpretation of the origin of petroleum. It is supposed that the decomposition of the residual animal fats is aided by certain ferments as yet not studied—anærobic bacteria analogous to those which have been studied in the cases of the transformation of wood into coal, the fermentation of cellulose, peat, etc.; the hydrogen sulphide formed at the bottom of the sea would be a product of the fermentations due to these bacteria.

Walden (1910) and Rakusin (1905 and 1906) made a new contribution to the explanation of the origin of petroleum, by discovering in various petroleums a slight optical activity, undoubtedly due to substances of organic origin (animal or vegetable). Neuberg (1905–1907) has shown that, in the putrefaction of protein substances (due, according to Effront, to the action of proteolytic enzymes generated, together with amidases, by micro-organisms, *see later*, Alcohol and Enzymes), marked quantities of optically active acids and amino-acids are formed, and by heating under pressure or dry-distilling a mixture of oleic acid with a little valeric acid, a product is obtained which, after purification, has the characters of naphtha as regards the optical rotation, boiling-point, and other properties. All this supports the organic—probably animal—origin of petroleum, and even if the fats do not give an optically active petroleum, the activity would be imparted by the decomposition products of the proteins. The optical activity of petroleum was recognised as far back as 1835 by Biot, who, however, drew no practical or theoretical conclusions from the observation. Rakusin observed that petroleums exhibit the *Tyndall phenomenon* (Vol. I., p. 107) to a more or less marked extent, and since petroleums are sometimes inactive and have varying chemical composition, he regards the different hypotheses concerning their origin as justified. Petroleum, as a liquid, must be considered as intermediate to natural inflammable gas and solid asphalte or ozokerite. Since the white *cerasin* which is extracted from *ozokerite* is *dextro-rotatory*, it must be concluded that ozokerite is of organic origin (the products formed by synthesis from simpler or artificial substances being optically inactive, *see* p. 23).

The petroleum or similar substances prepared artificially from the elements possess all the properties of true petroleum, but are optically inactive. Hence the most certain criterion of the organic origin of a petroleum is its optical rotation. If a petroleum is

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[1] **Fishing Industry.** The following statistics represent the mean annual figures for the period 1908–1914, and refer to both sea and fresh-water fishing:

	Number of fishing vessels.		Number of fishermen.	Value of fish caught (£).
	Steam.	Sailing.		
Great Britain	2,200	—	106,000	11,800,000
France	170	26,000	96,000	4,600,000
Norway	175	—	100,000	3,120,000
Spain	320	22,500	121,000	3,000,000
Germany	308	15,000	29,800	3,320,000
Holland	80	5,300	21,000	1,800,000
Denmark	160	1,000	14,000	640,000
Italy	—	25,796	110,000	1,360,000
United States	4,899	83,800	219,000	12,000,000

To obtain an idea of the fertility of certain fish, the *shad*, a fish of the herring family, weighing up to 5 to 6 kilos, may be considered; the female lays as many as 100,000 eggs, which may be fertilised artificially, as is done with the salmon and trout. In North America the eggs are collected and despatched to the Central Pisciculture Station at Washington, where they are hatched in four days in Macdonald or Weiss tanks with flowing water at 18° to 19°, and are immediately placed in the rivers, where they grow rapidly. Every year more than 100,000,000 eggs are fertilised in this way and from 1875 to 1890 the shad fishing showed an increase of 100 per cent., corresponding with £160,000. The female cod may lay as many as 6,000,000 eggs during its lifetime, and the turbot even 9,000,000; an adult eel contains 10,000,000 to 12,000,000 eggs.

optically inactive, it may have originated from a *racemic* product (optically and transitorily inactive, *see* p. 21) of organic origin, but may have been formed from inorganic materials. However, inactive petroleums are rare; Rakusin (1907) has found only three such up to the present, one Russian (Surakhany) and two Italian (Montechino and Velleia), and he states that not only the degree of carbonisation of the petroleum (richness in carbon), but also its degree of racemisation must be taken into account in judging its geological age.

In 1908, Zaloziecki and Klarfeld held that the optical activity of petroleum is due to the presence of terpenes or colophony, but Neuberg regards it as due to decomposition products of amino-acids (valeric or isocaproic acid) formed from the proteins. Marcusson (1908) combats the last two hypotheses, and shows that it is more probable that the activity is derived from decomposition products (dextro-rotatory) of lævo-rotatory cholesterols (and hence of animal origin, whilst the vegetable ones are dextro-rotatory and yield lævo-rotatory decomposition products). By distilling olein under pressure, Marcusson (1910) obtained hydrocarbons which had an optical activity equal to that of natural petroleums and which he regarded as formed from the original cholesterols. By the action of ozone, Molinari and Fenaroli (1908) showed that the Russian and Roumanian petroleums examined by them contained no *unaltered* cholesterol, but this does not exclude the presence of active decomposition products, which, however, would not contain double linkings. C. Engler and Bobrzynski (1910) confirmed these results. In addition to dextro-rotatory compounds, Java and Borneo petroleums contain lævo-rotatory substances which become dextro-rotatory at 350° (as happens when lævo-rotatory cholesterol is heated); also certain inactive fractions become dextro-rotatory when heated. Rakusin, Molinari, and Fenaroli showed that the optical activity increases in those portions of petroleum that have the highest boiling-point. Charitschkov (1912) supposes petroleum to be derived from asphalte.

COMPOSITION AND PROPERTIES OF CRUDE PETROLEUM. As obtained from the wells, crude petroleum varies in colour from yellowish to pale brown, or even black, according to its origin; it exhibits a marked greenish fluorescence and a characteristic, garlic-like odour. The dissolved gas soon separates spontaneously, and sometimes, on oxidation in the air, petroleum deposits dark, bituminous substances (paraffin wax, tar). The lighter petroleums are the paler and have an agreeable, ethereal odour, whilst the heavier ones are darker and have an unpleasant odour.

Certain petroleums have recently been found to be radioactive.

The presence of sulphur in petroleum, even if much less than 1 per cent., injuriously affects its odour and colour. The specific gravity of petroleum varies from 0·780 to 0·970. Petroleum obtained from Terra di Lavoro, Italy, has a high specific gravity (0·970) and certain Roumanian and Indian petroleums, rich in paraffin wax, show values higher even than this, sometimes as much as 1·3.

Petroleum is soluble in ether, benzene, chloroform, and, to some extent, in amyl alcohol; it dissolves only slightly in ethyl alcohol and not at all in water.

The *specific heat* varies from 0·4625 to 0·4724, that of light benzines being about 0·4840, that of heavy benzines 0·4679, that of masut 0·5010, and that of oil of paraffin 0·5424. The *coefficient of expansion* is 0·00063 and the *heat of combustion* 10,000 to 11,500 Cals., that of paraffin wax being about 11,000 Cals.

The *heat of evaporation* (*i. e.*, the heat necessary to transform 1 kilo of liquid at the boiling-point into vapour at the same temperature) varies with the density of the different fractions; for a product of density 0·640 and b.-pt. 40°, it is 80·6 Cals., for one of density 0·743 and b.-pt. 93°, 68 Cals., and for one of density 0·813 and b.-pt. 176°, 51·6 Cals.

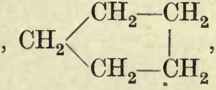
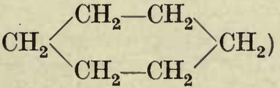
Montechino petroleum has the sp. gr. 0·740; that of Velleia, 0·780; American, 0·800 to 0·870; Russian, 0·850 to 0·900; and Galician, 0·827 to 0·890.

Different petroleums are composed, as a rough mean, of 13 per cent. of hydrogen and 87 per cent. of carbon, small proportions of oxygen, nitrogen, and sulphur compounds being also present. The hydrocarbons present in petroleum are numbered by the hundred, and they belong to different series, one or other of which preponderates according to the source. Thus, Pennsylvanian petroleums are constituted almost exclusively of hydrocarbons of the saturated series C_nH_{2n+2} (derivatives of methane), which are also found in Galician petroleums, etc.

Some petroleums contain as much as 40 per cent. of hydrocarbons solid at the ordinary temperature (paraffin wax), and these are left after distillation (*e. g.*, Java petroleum); usually, however, much less than this is present, American petroleums having only 2·5 to 3 per cent., and those of Baku sometimes only 0·25 per cent. Different petroleums may be distinguished by means of the ultra-microscope, the paraffin wax being dissolved in the colloidal condition.

It is maintained by various chemists that the paraffin wax is not pre-existent in petroleum, but is formed during its distillation. This is contradicted by the fact that some petroleum pipes show deposits of paraffin wax, and this may also be separated from cold petroleum by special solvents.

Hydrocarbons of the *unsaturated ethylene* series, C_nH_{2n}, preponderate in the petroleums of Burma and are abundant in those from California; Pennsylvanian petroleum contains about 3 per cent. Different petroleums may hence be distinguished by the quantities of bromine or iodine which they fix, by the amounts of hydrobromic or hydriodic acid then formed (Park and Worthing, 1910) or by the quantities of ozone they take up (Molinari and Fenaroli, 1908).

Hydrocarbons of the same general formula, C_nH_{2n}, but *saturated* (cyclic compounds, so-called *naphthenes*, or derivatives of *cyclopentane*,  $CH_2\left\langle\begin{matrix} CH_2-CH_2 \\ \qquad | \\ CH_2-CH_2 \end{matrix}\right.$, or *cyclohexane*,  $CH_2\left\langle\begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix}\right\rangle CH_2$) form 80 per cent. of Baku petroleums and occur abundantly in those of Galicia, together with about 10 per cent. of hydrocarbons of the aromatic series [recently (1910) *hexahydrocumene* has been identified].

Borneo petroleum contains up to 5 per cent. of toluene and also benzene, and these were utilised by the French and British during the war to prepare toluene for making explosives.

In a Russian petroleum and also in a Roumanian one, Molinari and Fenaroli (1908) found hydrocarbons derived from naphthenes with two double linkings and having the general formula C_nH_{2n-14} (for example, $C_{17}H_{20}$).

In certain petroleums small quantities of acetylene derivatives occur.

The *formolite reaction* [1] permits of the detection of unsaturated components,

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[1] The *formolite reaction* was suggested in 1904 by Nastjukov, who showed that, when treated with formaldehyde and sulphuric acid, all unsaturated cyclic compounds, that is, benzene derivatives and alicyclic derivatives containing at least one double linking, give an insoluble, complex condensation product or formolite, which contains C, H, O and S (*see* Baekelite). This reaction is used to separate from mineral oils cyclic compounds with double linkings. To the mineral oil, dissolved in twice its quantity of petroleum benzine, is added an equal weight of concentrated sulphuric acid, the mixture being then cooled, shaken with one-half its weight of 40 per cent. formaldehyde solution, and, after half an hour, poured into six times the weight of ice water; the liquid is then filtered and the insoluble matter dried and weighed. Russian mineral oils give 10 to 24 per cent. of formolite and the American oils 30 to 33 per cent., whilst lubricating oils yield no formolite.

The *reaction with nitric acid* (Marcusson, 1911) also throws light on lubricating mineral oils: 10 c.c. of the mineral oil is dissolved in petroleum benzine (b.-pt. below 50°), and the solution added in drops to 30 c.c. of fuming nitric acid cooled to − 10°, 50 c.c. of concentrated (not fuming) nitric acid at − 10° being afterwards added and the whole introduced into a separating funnel. Three layers are thus formed: the lowest, acid layer contains all the compounds soluble in nitric acid and the uppermost, benzine layer all the compounds not attacked by the nitric which may also be determined by means of the *iodine number* (*see later:* Fats and Oils), this being 3·3 to 6 for Russian and 8 to 15 for American petroleum.

It is found that petroleums produced in localities relatively near to one another often have different compositions; according to David Day this is due to the fact that the unsaturated hydrocarbons diffuse less easily through sandy or other soils, and this system of natural filtration gives rise to various types of petroleum, with preponderance of saturated hydrocarbons in some and of unsaturated hydrocarbons in others. These separations depend on the different surface tensions of the various components, as well as on the varying attraction and surface action exerted by the filtering material. This explanation is more reasonable than that the separation has been effected by distillation.

The products that distil below 180° are almost exclusively saturated and those distilling about 200° mostly unsaturated.

The very small quantities of *oxygenated* substances contained in petroleum (often less than 1 per cent. and rarely 5 per cent.) are composed of phenols and organic acids (*e. g.*, in Galician petroleum).

The traces of nitrogenous substances found in various petroleums (*see above*) support the hypothesis of the organic origin of petroleum.

Almost all petroleums contain *sulphur*, which is very difficult to remove and imparts an unpleasant odour and bad colour.

Usually the proportion of sulphur is about 0·10 to 0·15 per cent., but the petroleum of Terra di Lavoro contains as much as 1·3 per cent., while still more is found (up to 3 per cent.) in those of Texas, Ohio, Indiana, and Virginia, from which it has to be separated (*see later*).

The nature of the sulphur compounds present has not yet been completely defined, but the presence of mercaptans, thio-ethers, and thiophene and its homologues (methyl- and dimethyl-thiophene) has been detected. According to Heusler it is only necessary to heat a little of the petroleum with a granule of aluminium chloride to detect the presence of sulphur, hydrogen sulphide being then developed.

Also by fractional distillation and partly by the specific gravity, the four principal types of petroleum may be distinguished. The products distilling below 150° form the *benzines* (*see later*), then up to 280° are obtained *lighting oil* or *solar oil* (or *kerosene*), and after 300° remain products used for the extraction of paraffin wax and vaseline (American) or for the preparation of *mineral lubricating oils* (Russian):

Crude petroleum.	Specific gravity.	Benzine.	Solar oil.	Residue.
Pennsylvania [1]	0·79–0·82	10–20 %	55–75 %	10–20 %
Ohio	0·80–0·85	10–20 %	30–40 %	35–50 %
Caucasus	0·85–0·90	0·2–5 %	25–30 %	60–65 %
Roumania	0·85	3–10 %	70–80 %	10–15 %
Galicia	0·82–0·90	5–30 %	35–40 %	30–50 %
Italy (Piacenza)	0·74–0·79	25–40 %	55–65 %	4–8 %
Alsace	0·912	5 %	35–70 %	55–60 %

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acid; the intermediate, oily layer is small (3 to 5 per cent.) and of a blackish-brown colour. The bottom layer is dropped on to ice, a solid, yellow substance (aromatic and other nitro-derivatives) separating, which is collected on a filter, dried and weighed. The top layer is heated to expel the benzine, the paraffins, naphthenes, and polynaphthenes then remaining.

With formolite there separate the cyclic, aromatic, and alicyclic compounds, while nitric acid acts on all unsaturated (cyclic and aliphatic) compounds. American mineral oils give larger proportions of nitrated products than the Russian (these are more resistant to the action of nitric acid). The formolite reaction separates the less viscous products (less lubricating), whilst nitric acid acts also on viscous components of good lubricating properties (olefines and possibly polynaphthenes to some extent).

[1] The varying nature of American petroleums is shown by the following results: Pennsylvanian and similar petroleums yield 60 per cent. of lighting oil, 12 per cent. of benzine, 12 per cent. of lubricating oils, 12 per cent. of fuel oils, and 1·5 per cent. of paraffin wax, whilst Californian petroleums give 13 per cent. of lighting oil, 5 per cent. of benzine, 51·4 per cent. of lubricating oils, and 30 per cent. of fuel oils (considerable losses occur during the refining of Californian petroleum). These figures show why crude Pennsylvanian petroleum costs three times as much as that from California.

In some of the islands of the Caspian Sea (Tscheleken) is found a petroleum resembling the American type, with a large proportion of paraffin wax (5·5 per cent.), and in Columbia (S. America) petroleums like those of Russia (Caucasus) occur.

The *Italian petroleums* vary considerably in composition and those of Emilia and Piacenza are so pale and so rich in benzine and poor in residues that it is supposed that they are the condensed or diffused (*see above*) more volatile products of more important deposits not yet discovered. In the distillation of the Velleia petroleums at Fiorenzuola d'Arda the little residue obtained is added to the crude petroleum to be refined and thus becomes distributed in the lighting oil, so that the less remunerative residues are never placed on the market. The absence of optical activity in the petroleums of Montechino and Velleia (*see above*) seems to confirm the view that they are derived from more important deposits, in which optically active products would probably be found.

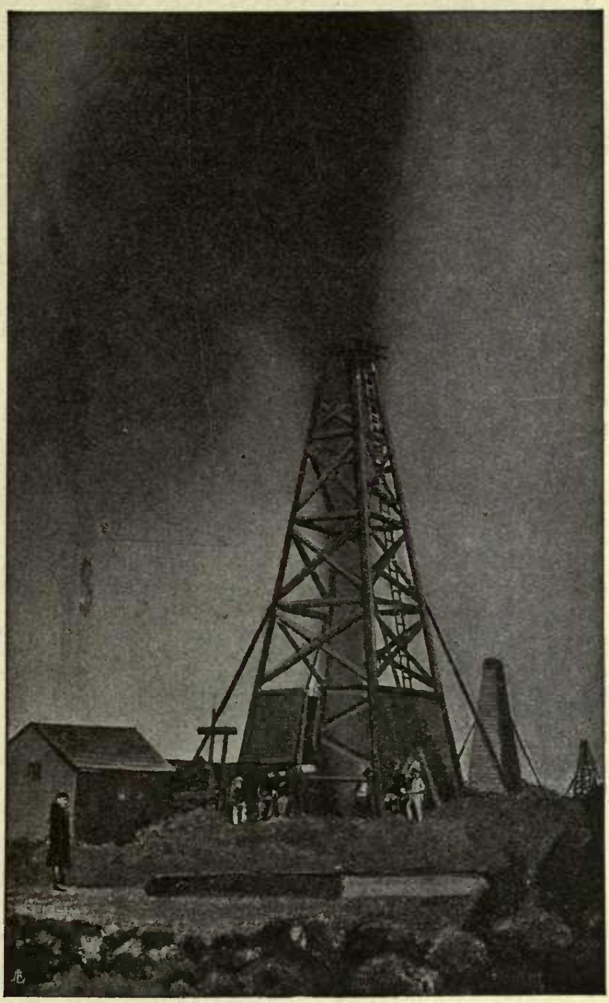

FIG. 80.

EXTRACTION AND INDUSTRIAL TREATMENT OF PETROLEUM. From the most remote times petroleum has been raised in China by means of wells similar to the present artesian ones, which the Chinese used many centuries before Europeans for obtaining drinking water. In other regions in times gone by the petroleum flowing at the surfaces of the water-courses began to be separated and used; then wide, shallow wells were dug and the petroleum raised to the surface in buckets. Nowadays, however, petroleum is everywhere obtained by wells bored into the earth like artesian wells, and sometimes the petroleum flows to the surface under great pressure, so that it forms a fountain (*see* Note, p. 74, and Fig. 80). It is supposed that the deposits of petroleum in the interior of the earth's crust are situated in large cavities or pockets, where there is often a lower layer of salt water (Fig. 81, W) and on this floats a more or less abundant layer of petroleum E; in general, the upper part of the pocket is filled with inflammable gas, G, which exerts great pressure. If the boring, B, reaches one or the other layer, one or the other product is obtained in preponderance or even exclusively, and, after the aqueous layer is exhausted, the same well may yield only petroleum.

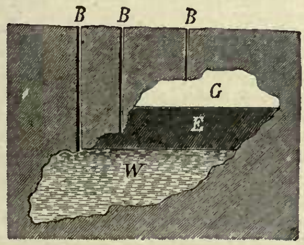

FIG. 81.

The sinking of a well is begun with a boring 35 to 40 cm. in diameter by means of suitable boring tools worked by long rods and toothed gearing, or by compressed-air drills mounted on wooden structures termed *derricks* (Fig. 82); the detritus of the bored rock is continually carried away from the boring by a current of water, whilst in former times the much slower dry boring was preferably employed. When the petroleum layer is approached, the water of the well or tube begins to show drops of petroleum. The power is often supplied by portable steam-engines, which should not be placed too near the boring, since if the petroleum or gas escapes accidentally in any quantity during the boring, it may ignite and cause considerable damage by fire or explosion.

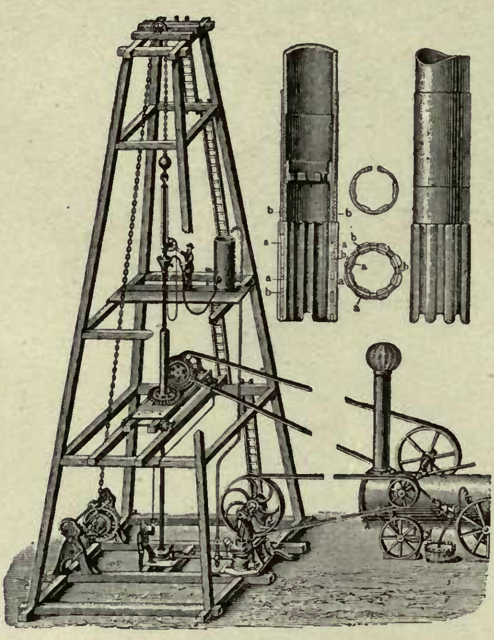

Fig. 82.

In such cases it is hence advisable to transform the energy on the site, for instance, with electric motors. Even then fires and explosions have been caused by the accidental ignition of the gas mixed with air, by sparks formed by stones, issuing violently from the well along with sand and petroleum and striking the iron framework or the rails of the woodwork.[1]

When the petroleum is not exuded under pressure, it is often raised by means of pumps, but this is not possible where much sand (up to 30 per cent.) is also extracted and has to be allowed to deposit; this is the case at Baku, where, however, one-third of the petroleum issues under pressure.

During recent years there have remained relatively few "fountains" at Baku, and the petroleum of the sandy wells, which cannot be raised by pumps, is extracted

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[1] Artesian wells for extracting petroleum have an average diameter of 25 to 50 cm., and vary in depth according to the region; at Baku they were first of all 60 to 150 metres deep, but of recent years wells have usually been sunk to a depth of 250 to 350 metres (occasionally 1000 metres). In the Washington district of the United States the wells are from 700 to 850 metres deep, and near Pittsburg is the deepest of all, 1820 metres. The wells are 100 to 200 metres apart according to the locality, and they remain active for five to ten years.

The cost of boring varies with the district, that is, with the nature of the subsoil, and, under favourable conditions and for wells not too deep, each boring costs about £400. Those made in the Washington district cost even £1400 to £1600. At Velleia, in the province of Piacenza, the wells are little more than 100 metres deep, whilst at Salsomaggiore they have been bored to a depth of 400 metres, and in one case of 700 metres, in order to utilise for medical purposes the iodine-salt water which is obtained, together with a little petroleum. In America the well is widened at its lowest point, where it meets the petroleum, by exploding a dynamite cartridge ("torpedoing").

A well sunk in 1891 at Balakhany, 270 metres deep, gave an uninterrupted jet producing 3276 tons of petroleum per twenty-four hours, and the mass of sand expelled covered the whole neighbourhood. A little distance away one of the Nobel Company's wells, in 1892, gave 13,000 tons per day. In February 1893 a well was sunk at Romany, near Baku, which for several weeks yielded 10,000 tons of petroleum per day; the oil issued from the earth with such violence that the movement of the air broke the windows of neighbouring houses, and, as at first it was not possible to guide the jet into horizontal channels, all the iron plates used for this purpose being pierced, 250,000 tons of petroleum were lost in five weeks. In 1909 a new well at Baku gave, for a long time, 3500 tons of naphtha per day. A well bored at Maikop (70 kilos from the Black Sea), on September 12, 1910, to a depth of 70 metres, gave a jet 64 metres above the surface of the ground and a production of 6000 tons in twenty-four hours; on September 18 the fountain caught fire and five days passed before it could be extinguished.

Fountains as rich as this are exceptional; usually wells yield much less, and at Baku a well is generally abandoned when it gives less than four tons in twenty-four hours. In Italy, however, wells are used which give only a few hundredweights of petroleum per day; some of the Italian wells produce only 60 litres a day, others as much as 2500 litres or more.

by special "bailers" made of a cylinder of sheet-metal terminating in a cone and fitted in the lower portion with a valve which opens when the bailer (called the *shalonka*) becomes immersed in the petroleum and closes on raising by means of pulleys and windlass, the steel rope carrying the bailer being wound round a large drum a short distance from the well. The shalonka, containing some hectolitres of petroleum, is discharged by inverting it over a channel.

From the large masonry or clay reservoirs near the wells, the petroleum passes by means of iron pipes to the iron tanks (holding 5000 or even 10,000 cu. metres) of the refineries or to the despatching stations (suitable trains or vessels), which at Baku are very near, but in America some hundreds of miles from the wells; these pipes then traverse plains, mountains, and valleys, and in the same way and with the help of powerful pumping-stations, the refined petroleum is despatched to the place of loading. In 1905, the Standard Oil Company began the construction of another such pipe (*pipe-line*) to connect the works at Kansas City with the coast; the distance is about 1700 miles and the construction cost £880,000 and served to transport daily from 10,000 to 15,000 barrels of petroleum.[1]

To protect stores of petroleum from lightning and fire the same precautions as for explosives are employed (*see later*), while the tanks are so constructed that, in case of fire, streams of burning petroleum cannot reach other places.

DISTILLATION. Crude petroleum cannot be used for lighting, as it has a bad smell and colour, contains many impurities, and is composed partly of excessively volatile products, which might easily cause explosions or fires in the lamps. In order to avoid these dangers, the petroleum is subjected to exact refining, which is controlled by legal enactments and with special apparatus (*see later*).

The refining is carried out in a manner which varies with the nature of the petroleum and usually consists of a fractional distillation and a chemical purification.[2]

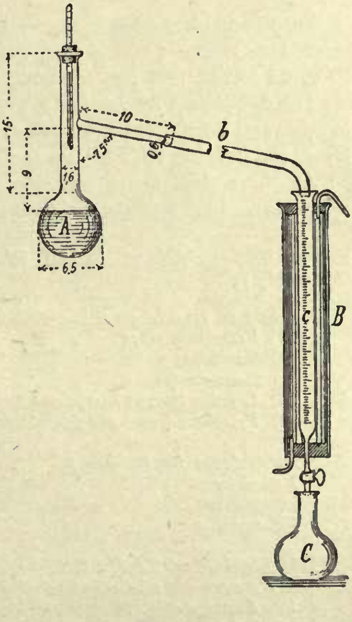

Fig. 83.

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[1] The problem of *transporting petroleum to great distances* through pipes is far more complex than it seems at first sight. The capacity of a pipe is proportional to the square root of the fifth power of the diameter and depends on the pressure of the pump, the length of the pipe, the differences of level to be overcome and the viscosity of the liquid. Transport difficulties encountered especially with petroleums very rich in bituminous substances and very dense, were overcome when it became possible in America to make homogeneous iron pipes eight inches in diameter and capable of resisting pressures of 60 to 105 atmospheres. Recently, however, it has been shown by Isaac and Buckner Speads that admixture of 10 per cent. of water with the petroleum diminishes the friction in the pipes to an enormous extent, especially if the inner surface of the pipe is given a spiral form; the liquid then assumes a rotatory movement with the water at the periphery, so that the friction of the petroleum is exerted on the water and not on the surface of the pipe. To prevent stoppage of the pumps from causing the establishment of an uninterrupted column of petroleum, which would produce considerable friction on resumption of working, the pipe is made undulating; the water then collects in the depressions.

If p denotes the loss of power in a pipe 100 feet long, d the diameter of the pipe, y the velocity in feet per second, and k a constant, then $p = d\ k\ y^2$. Experiment shows that for a *smooth* 8-inch pipe with pure petroleum, $k = 70$, and with petroleum and 10 per cent. of water $k = 41$, whilst with a pipe having a spiral inner surface (with 10 per cent. of water), $k = 0{\cdot}37 - 0{\cdot}49$. Through one and the same pipe petroleums and oils of different qualities may be passed successively without danger of mixture, owing to the high pressure in the pipe. This is explained by the fact that, while the 10 per cent. of water is transported with some degree of friction, the 90 per cent. of petroleum, which does not mix with the water, slips and glides over the latter with extraordinarily little friction.

[2] The fractional distillation in the laboratory is carried out in Engler flasks (Fig. 83), which are of definite size and shape and permit of concordant

The *industrial refining* of petroleum consists in separating the crude petroleum into these three groups, I, II, and III.

Apparatus is used for discontinuous, or for continuous, distillation.

Discontinuous distillation is conveniently carried out in the so-called *waggon-still* largely used in America and at Baku. It holds as much as 2500 barrels at a time (Figs. 84 and 85).

It is made of wrought-iron 10 to 14 mm. in thickness, and has a corrugated bottom; it is commonly 7 metres long, 4 metres wide, and 3 metres deep. The top is fitted with three flanged elbows which carry off the vapour. In thirty hours three distillations can be carried through, the residues being discharged through the three orifices, *c*. The heating is effected by means of these residues, which are forced into perforated pipes, *r*, in the double-arched hearth; rational circulation of the products of combustion results in effective utilisation of the heat.

More profitable use is now made of simpler, cylindrical boilers, which, although of larger dimensions, correspond almost exactly with the various types of steam-boilers, the heating being external, or lateral, or internal, or two of these together. Such boilers of 600 to 700 or more barrels capacity are commonly used even in America, where, however, both the more complex and more perfect Lugo apparatus and the Rossmässler apparatus, in which the heating is effected by superheated steam, are also employed.

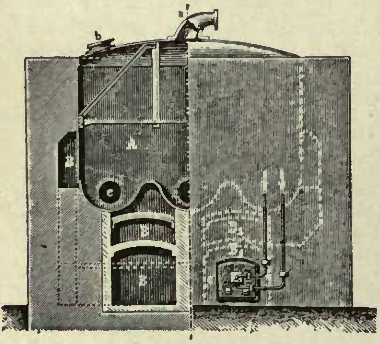

Fig. 84.

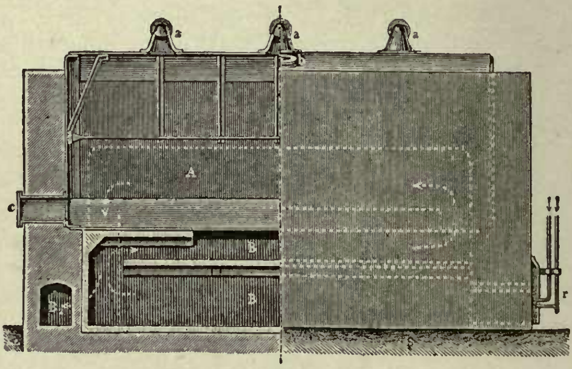

Fig. 85.

For the condensation of the vapours that distil over, complicated iron coils are arranged in cisterns through which cold water circulates continuously, the bore of the pipe being 20 to 25 cm. at first and gradually diminishing to 5 to 8 cm.

The distillate with specific gravity not exceeding 0·750 and b.-pt. 150° forms the crude benzine and is collected and worked up separately. The distillate with sp. gr. 0·750 to 0·860 forms the lighting oil, and the *residue* is treated separately.

At the end of the distillation, decomposition of the substances of higher molecular weight is avoided by direct injection into the mass of superheated steam (in many American

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results being obtained in all laboratories; the following fractions are then weighed separately:

	Boiling-point.	Specific gravity.
I. *Light or readily volatile petroleums:*		
(*a*) *Petroleum ether*	40–70°	0·635–0·660
(*b*) *Gasolene*	70–80°	0·660–0·667
(*c*) *Benzine*	80–100°	0·667–0·707
(*d*) *Ligroin* (burnt in special lamps for lighting) .	100–120°	0·707–0·722
(*e*) *Petroline* (used for de-fatting or cleaning) . .	120–150°	0·722–0·737
II. *Petroleum for lighting:*		
I quality	150–200°	0·753–0·864
II quality	200–250°	
III quality	250–300°	
III. *Residues of the distillation:*		
(*a*) *Heavy oils:* lubricating oils	above 300°	0·7446–0·8588
(*b* *Paraffin oil*		0·8588–0·9590
(*c*) Coke		

factories, however, decomposition of these products is purposely effected, *see later*), so that heavier lamp oils distil and condense with the water, while the residue (masut) is better suited to the preparation of heavy cylinder oils. This masut is then distilled in other stronger vessels under reduced pressure (*see later :* Lubricating Oils) and with superheated steam at 400°, yielding a distillate of medium oils easily separable from the water and a *vacuum-concentrated residue* serving for the preparation of an excellent *dark cylinder oil*, which has a flash-point above 280° and contains paraffin wax in the colloidal state.

Continuous distillation is employed more especially at Baku, with large plants consisting of boilers arranged in series so that each boiler is maintained at a definite, constant temperature, the vapours passing from one boiler to the other only depositing in a condensed form those portions corresponding with a given boiling-point and a given specific gravity. By feeding the first boiler—which is at the highest temperature—continuously, the others are also fed indirectly and kept full, each of them discharging a fraction of a definite, constant specific gravity. Naturally the higher temperature boilers are furnished with *dephlegmators* (Fig. 86), which cause ready deposition of the heavy oil carried over with the very hot vapours. In these boilers the heating or distillation is effected by means of *superheated steam*, which is usually obtained by passing steam from a boiler (*D*, Fig. 87) through a series of iron pipes heated in a furnace by direct-fire heat.

In addition to other advantages, continuous distillation gives an increase of 30 per cent. in the amount of lamp oil. The residue left after distilling the crude petroleum up to 280° bears the Tartar name of *masut* or the Russian one of *astatki* (*ostatki*). The amount of petroleum distilled in twenty-four hours corresponds with four times the capacity of all the boilers in the battery.

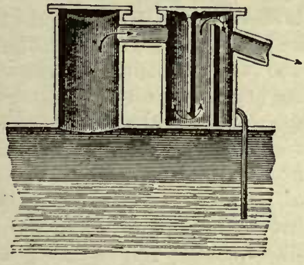

Fig. 86.

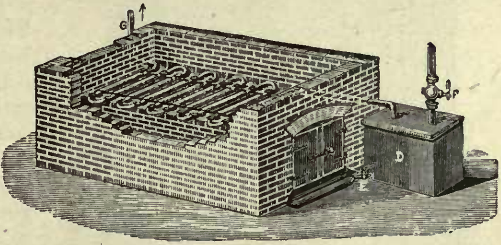

Fig. 87.

The Nobel Company at Baku has boilers which distil 1000 tons of petroleum in twenty-four hours. During recent years rectifying columns similar to those used for alcohol have been employed, these admitting of a large production without the use of large boilers.

In the "Black Town," near Baku, there are 200 refineries, which treat the whole of the petroleum of the district. The odour of petroleum is perceptible at a great distance, and the town is always covered and surrounded with dense, black smoke. The most important refinery is that of Nobel Brothers, which refines one-half of the annual output of the Caspian, although this firm possesses only one-eighth of the total number of wells.

The *Kubierschky column* (*see later :* Benzine) does not appear to be suited to the distillation of petroleum. In distilling crude petroleum at Baku, as much as 5 per cent. of fuel (heavy oils or residues) was at one time used, but the mean consumption was 3·85 per cent. in 1909 and 3·42 per cent. in 1911, and under the most favourable conditions was only 2·5 per cent.; still greater economy might, however, be effected. To distil Surachany petroleum 19,627 Cals. are required per 100 kilos, but during the condensation 17,359 Cals. are recoverable.

The Bayonne works of the Standard Oil Company at New Jersey deals with raw petroleum comparatively poor in benzine and lamp oil and rich in heavy oil. Since the lighter products are preferred, the crude oil is subjected to an initial distillation, which is prolonged as far as the final products. Two qualities of lamp oil (sp. gr. 0·730 to 0·807 and 0·800 to 0·808) are collected separately, and direct superheated steam is used to raise the temperature to 350° or even 390°; a mixture of equal parts of water and a dense medium oil (sp. gr. above 0·850, viscosity 3 at 20°) is thus obtained which is of poor quality as lighting or lubricating oil, but serves for making oil-gas (*see* p. 64) by dropping it into red-hot retorts, and also for carburetting water-gas and for gas-engines. The temperature is then raised still higher without evacuating and without the use of steam, this being a modified form of "cracking" (*see later*); the vapour distilling from the large, horizontal, iron vessels used passes into a dephlegmating column filled with stone situate above, the products of higher boiling-point being condensed and returned to the vessel to undergo further decomposition, whilst the vapours of the lighter products pass to the condensers. The heating is carried out by means of small anthracite, which is more economical than using petroleum residues, as is practised in Russia and Austria. The heavier products which distil last are naturally kept separate from the raw petroleum distilling first and from the benzine, and the distillation is continued until oil rich in paraffin wax no longer distils over and there remains in the still *petroleum coke,* which is used for making arc-lamp carbons. These last oils are intensely cooled with brine from a refrigerating machine (*see* Vol. I., pp. 260, 621), this circulating round large, horizontal iron cylinders, through which the oil is transported from end to end by means of a revolving vaned shaft; the oil, which is thus cooled to 4° to 5° and then exhibits the consistency of butter, is next passed into large filter-presses, these retaining the *paraffin wax* in cakes (*see later*). The dense oils passing through the filters serve for the manufacture of lubricating oils.

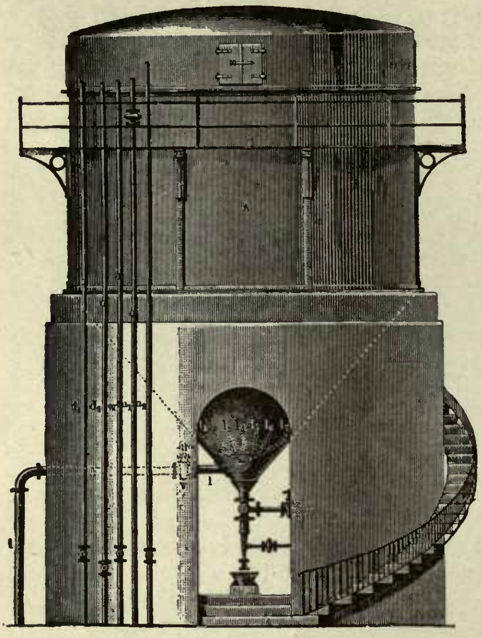

FIG. 88.

CHEMICAL PURIFICATION OF PETROLEUM. The petroleum distilling between 150° and 300° is not yet suitable for lighting purposes, as it has a marked, rather unpleasant odour and a faint yellow colour, and contains substances which detract from its value. It was Eichler at Baku who first suggested (1865) purification by means of concentrated sulphuric acid.

This is carried out in large iron tanks with conical bases (Fig. 88), the petroleum being treated with several separate quantities (altogether 1 to 3 per cent.) of concentrated sulphuric acid of 66° Bé. (nowadays the monohydrate obtained by the catalytic process), the mixture being vigorously agitated by compressed air blown in at the bottom of the tank, and each quantity of the acid separated after half an hour's rest. The first addition of about 0·5 per cent. of acid serves also to dry the petroleum, the remainder being added in two portions.

The sulphuric acid acts especially on the aromatic hydrocarbons (forming sulphonic acids), the olefines and the oxygenated acid compounds, as well as on the colouring and sulphur substances. The sulphuric anhydride attacks also the naphthenes to some extent. Sulphuric acid has a polymerising action, so that a small part (1 to 3 per cent.) of the petroleum is resinified and the acid is turned black by the dissolved resins, but may still be used for the manufacture of superphosphates.[1] In order to weaken the action of the acid some-

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[1] According to Ger. Pat. 221,615 of 1909 this black acid, containing sometimes as much as 2·5 per cent. of complex organic substances, may be purified by causing it to fall into pure, boiling sulphuric acid through which a current of air is passed; all the acid distilling over is then pure and colourless. In California the refineries use oleum, and the black acid recovered is mixed with coke or other suitable, readily oxidisable organic substances and heated, most of the sulphuric acid being converted into sulphur dioxide, which is then used for making catalytic oleum. In some refineries the black acid is poured carefully into about an equal weight of water (giving an acid of 30° Bé.), the tarry mass then separating at the surface being decanted off and utilised, and the residual acid either mixed with that used for the manufacture of superphosphates or heated at 140° to 150° in leaden vessels so as to concentrate it to 60° Bé., the tarry matters remaining dissolved being thus separated or carbonised. After being washed with water, the

what, it is mixed with sodium sulphate; further, in order that yellowing of the petroleum may be avoided, sulphuric acid containing less than 0·01 per cent. of nitrous acid should be employed. After the action of the acid, the petroleum is washed in lead-lined vessels thoroughly with water and then with 1 to 1·5 per cent. of concentrated caustic soda solution (20° to 25° Bé.), air being passed in from beneath to effect mixing; in this way the traces of acid remaining and also the phenolic compounds are removed. After the alkali has been separated, the oil is again well washed with water. The remaining petroleum is not clear, as it is emulsified with a little water, but it clarifies on standing or more rapidly on being filtered through sawdust and salt or Fuller's earth (*see* Vol. I., p. 738) by means of filter-presses, all traces of emulsion being thus removed.[1]

In recent years Edeleanu has applied in Roumania a new method of purifying very viscous petroleum residues by means of liquid sulphur dioxide, which very readily dissolves the unsaturated, carbon-rich hydrocarbons. The petroleum to be refined is dried by passing it through dry sodium chloride mixed with one-fourth of its weight of calcium chloride and is then cooled in an iron vessel to − 10°. Liquid SO_2 (one-fourth more in amount than the petroleum) at − 10° is then allowed to fall in a fine spray on the surface of the liquid, which is not mixed; in a short time two layers separate, the upper one consisting of petroleum saturated with SO_2, and the lower one of liquid SO_2 containing in solution the heavy unsaturated hydrocarbons and other impurities. This lower layer is removed as it forms to a tank where, at a rather higher temperature, it gives off the SO_2, this being again liquefied. The SO_2 dissolved by the petroleum is liberated similarly, the last traces of the gas (0·3 per cent.) being removed by washing with water. The residue of heavy, unsaturated hydrocarbons, mixed with tar and other impurities, is used as a substitute for oil of turpentine or heavy oils. This process requires somewhat complex plant.

In 1912 there were two large plants in Europe making use of this process, the loss of SO_2 being 0·05 per cent. on the weight of petroleum refined and the inclusive cost 6*s*. 10*d*. per ton. The plant necessary for the treatment of 65 tons of petroleum per ten hours costs about £10,000.

Attempts have been made, without any marked practical success, to purify petroleum by means of alcohol, hypochlorites, bisulphites, zinc chloride, etc.

Some crude petroleums give a rather yellow lamp oil, which is decolorised by exposure for some time to the sun in shallow tanks covered with sheets of glass. Sometimes the yellow tint is removed by dissolving in the petroleum traces of complementary blue or violet dyes; as, however, nearly all commercial dyes are insoluble in petroleum, it is necessary to obtain from the manufacturers the *bases* of the colouring-matters, these being soluble.

In certain cases, decolorisation is attained with infusorial earths, clays, or natural

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tarry mass serves either as a substitute for tar, or for impregnating timber, or as a fuel. Nitrogenous residues (waste horn, hides, leather) are sometimes converted into nitrogenous fertilisers (containing ammonium sulphate) by treatment with the hot, black acid.

According to F. Bräunlich (Ger. Pat. 267,873, 1913) it is better to add the black acid, not to pure acid, but to sodium bisulphate (or the potassium or ammonium salt, or a mixture of these) heated to fusion, pure sulphuric acid then distilling off. J. Fleischer (1907) obtains colourless acid (45° to 50° Bé.) by causing the black acid to diffuse through porous partitions washed by a little water.

The concentration of the acid cannot be determined by ordinary titration, since the sulphonic acids present also have acid reactions; these, however, yield soluble barium salts.

[1] The *black alkaline liquors* from the refining of petroleum may be utilised by concentrating them in iron pans to a syrupy consistency and calcining the residue in a muffle furnace; this procedure yields sodium carbonate, which is extracted with water and may be converted into alkali hydroxide by treatment with lime (*see* Vol. I., p. 554). Unsaturated hydrocarbons and ketones (acetone, etc.) may be condensed from the gases evolved from the muffle furnace.

The black alkali liquors may also be used for the preparation of the sodium salts of the *naphthenic acids* (*e. g.*, tridecanaphthenic acid; *see later, Naphthenes*), which are used as substitutes for *antiseptic soaps* and are obtained by heating the liquor in iron pans in which bags containing sodium chloride are immersed. The heating and concentrating are continued until sufficient salt is dissolved to cause separation of the sodium salt of the naphthenic acids. The alkaline salt solution is then decanted off and treated as described above, whilst the soap substitute is heated further until it gelatinises completely, and is then despatched in wooden casks; the product has a less disagreeable odour if a current of hot air or superheated steam is passed through the mass before the alkaline salt solution is separated.

The direct utilisation of the black alkaline liquor for the impregnation and preservation of railway sleepers has been suggested.

magnesium hydrosilicates (*Fuller's earth, see* Vol. I., p. 738), but these are not applicable to the dense, dark Californian petroleums.

A most important operation for petroleum rich in *sulphur* (present especially as H_2S) and hence dark and of unpleasant odour (like those from Canada, which can be used only as fuel and not for lighting purposes) is that of a *desulphurising* according to the process proposed by Frasch (1888–1893); this consists in distilling the petroleum with an excess of a mixture of metallic oxides—powdered copper oxide, 75 per cent.; lead oxide, 10 per cent.; iron oxide, 15 per cent. This operation reduces the sulphur-content from 0·75 per cent. or more to 0·02 per cent. It is calculated that, by this method, about 50 tons of sulphur are extracted daily from Ohio petroleum, most of it being lost.

The operation is carried out by simple *mixing* or by means of *vapour.* In the first case 6800 kilos (6·8 tons) of the oxide mixture are added to 200 tons of petroleum in a large tank, the mixture being subjected to prolonged agitation by mechanical stirrers, which keep the oxidising mass at the bottom of the tank in continual motion.

The petroleum is then decanted off into the fractional distilling apparatus, a second quantity of 200 tons of petroleum, together with 4500 kilos (4·5 tons) of oxides being added to the residue in the tank; the operation is repeated four or five times before renewing the oxides. The used oxides are regenerated by calcination, which removes the sulphur.

The Frasch process of desulphurising the vapour is far more rational and rapid; it consists in passing the petroleum vapours from the distillation vessel (from 100 tons of petroleum) (*A*, Fig. 89) successively into two communicating cylinders, *B* and *C*, placed one over the other and enclosed by a metal casing, *D*, above the boiler. The vapours pass first into the casing, next into the lower cylinder, and then into the upper one, coming into intimate contact with the mixture of metallic oxides, which is kept moving and subdivided in both cylinders by means of rotating reels, *h*, provided with peripheral brushes, *H*. The oxidising mixtures in the two cylinders are renewed alternately, while the purified vapours, after traversing a gravel filter, *G*, which retains particles of the oxides carried over, are condensed in ordinary coils, *F*. By this process, some refineries are able to purify as much as 11,000 tons of petroleum per day.

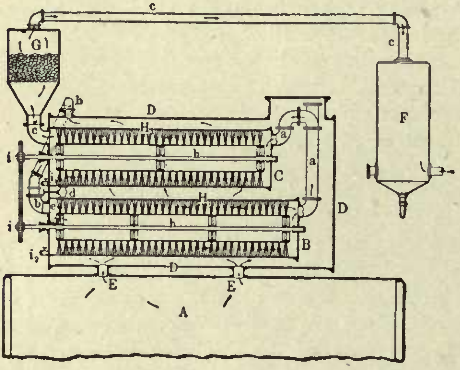

FIG. 89.

Recently petroleum has been desulphurised by means of metallic sodium, and treatment with aluminium chloride in the hot and under pressure is also recommended. V. Walker (U.S. Pat. 955,372, 1910) passes the vapours into columns fitted with perforated plates and containing anhydrous cupric chloride, the last traces of hydrogen sulphide being removed by passing the vapours into a solution of lead oxide in caustic soda. Robinson (1909) separates the sulphur by treating the petroleum with highly concentrated sulphuric acid.

In well-refined petroleums, the proportion of sulphur is always less than 0·06 per cent., usually 0·02 per cent.

Attempts are sometimes made to *deodorise* petroleum by addition of fatty acids and tannin and subsequent saponification, or by addition of calcium hypochlorite, or aluminium chloride, or bisulphites, or acetone, or formaldehyde. The odour may also be masked by addition of a perfume (bergamot oil, neroli oil, orange-flower oil).

The *fluorescence* may be eliminated by addition of yellow colouring matters (*e. g.*, nitronaphthalene, quinoline yellow, etc.).

PETROLEUM TANKS. The refined petroleum is preserved in large cylindrical sheet-metal tanks (Fig. 90), situated near the works; they are whitened outside to reflect the heat of the sun, and are furnished with charging and discharging pipes communicating with the pumping-station by which all the liquids in the works are circulated.

TRANSPORT OF PETROLEUM. For transport by land and sea, wooden casks holding 159 litres (about 145 kilos) were at one time exclusively used, but to-day land transport is effected by tank-cars (Fig. 91), which are now numbered in thousands (more than 20,000 in the United States, and more than 15,000 in Russia). For sea transport, tank-steamers are used (there are now 360 of these of the total capacity of 630,000 tons) (Fig. 92); when they arrive at their destinations in the ports of different countries, they are discharged by means of pumps into storage-tanks or directly into tank-cars. From these stores (there are tanks of 2000 tons capacity at Leghorn, Savona, Genoa, and Venice) the petroleum is despatched inland in wooden or iron casks or in cans holding 14 kilos (17 litres) and packed in pairs in wooden cases; the wooden casks are coated inside with a thin layer of glue.

For long-distance transport through pipes, *see* note on p. 75.

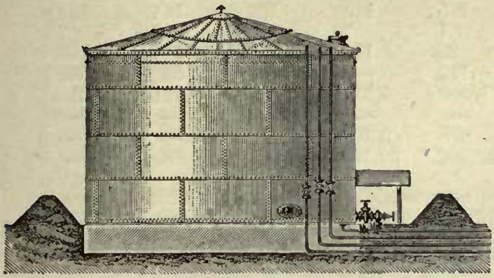

Fig. 90.

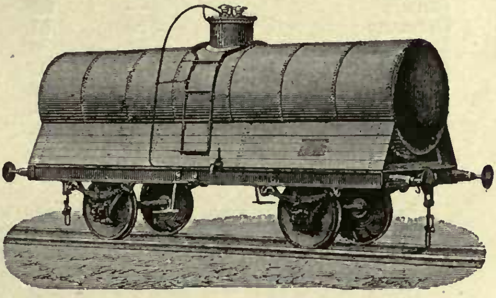

Fig. 91.

USES AND STATISTICS. The greater part of refined petroleum is still used for lighting purposes, either in the old lamps with flat wicks or in those with cylindrical wicks and flame-spreaders or in lamps with incandescent Auer mantles; it can be used advantageously for household illumination in town and country. Part of it is employed for power purposes, as in internal-combustion engines it gives an efficiency of 25 to 37 per cent., whilst coal yields only 12 per cent. However, while in Russia large quantities of petroleum were used in the past in factories and for locomotives, nowadays it is being replaced by coal; in America, on the other hand, the opposite is the case, and the Mexican Railway alone consumed more than 4000 barrels of petroleum per day for its locomotives in 1908. Its use on fast ships has the advantage of 28 per cent. saving in space. In America, about 19,000,000 barrels of petroleum were used altogether for railway locomotives in 1907. Lastly, it is used as a disinfectant and for lubricating engines, etc.

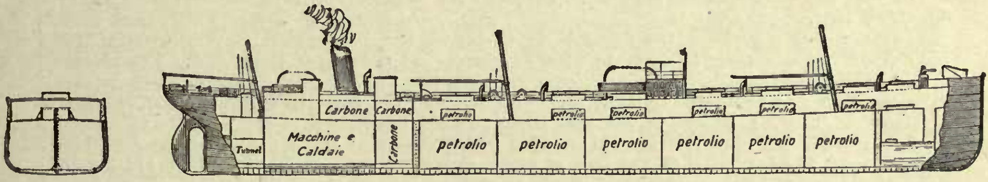

Fig. 92.

Carbone, coal; *petrolio*, petroleum; *macchine e caldaie*, engines and boilers.

The *production* of petroleum has increased in a surprising manner, in spite of the growing development of the gas and electrical industries. The following figures illustrate this for the two great petroleum-producing regions:

	Caucasus (Russia) Tons	United States Tons
In 1874	100,000	1,500,000
1884	1,500,000	3,400,000
1894	5,000,000	7,000,000
1905	7,969,239	17,636,000
1910	9,500,000	26,000,000
1916	9,934,000	40,100,000

The total *world's production* was about 12,000,000 tons in 1894, the output in succeeding years being shown in the note.[1]

[1] *Output of crude petroleum* (in thousands of tons):

	1900	1905	1910	1912	1913	1915	1916
United States . .	12,000	20,000	27,451	29,663	32,315	40,760	43,611
Russia	9,000	7,969	9,557	9,265	9,246	9,949	10,556
Dutch East Indies . .	800	1,126	1,495	1,520	1,534	1,793	1,910
Galicia	700	855	1,700	1,180	1,087	602	940
Roumania . . .	350	641	1,352	1,806	1,885	1,744	1,493
British India . .	300	600	818	900	1,000	1,189	1,231
Japan	120	195	270	250	250	452	434
Canada . . .	—	92	60	—	—	31	28
Germany . . .	59	81	145	140	130	144	144
Italy	23	6	7	7	6	6	7
Italy (importation) .	—	63	85	113	115	111	98
Peru	—	54	140	—	—	362	369
Mexico	—	—	1,600	2,100	3,000	4,771	5,628
Trinidad . . .	—	—	—	—	—	—	—
Various other countries .	78	85	673	2,375	3,350	—	—
World's output . .	23,000	31,000	43,500	50,798	60,000	66,880	—

In 1913, 63·8 per cent. of the total production of petroleum was due to the United States, 18·2 per cent. to Russia, 5·9 per cent. to Mexico, 3·7 per cent. to Roumania, 3 per cent. to the Dutch East Indies, 2·1 per cent. to Galicia, and 1·9 per cent. to British India.

Some of the Galician wells are 1200 metres deep and one as much as 1490 metres.

Great Britain imported 4269 tons of crude petroleum in 1909 and 674 tons in 1910, besides 528,545 tons of refined petroleum (£2,280,000) in 1909 and 500,000 tons in 1910.

In Germany the output of 145,000 tons in 1910 was furnished mainly by Hanover, next in order being Alsace (33,500 tons). Germany imported 983,500 tons of petroleum (31,500 of the crude product, which was refined in Germany) in 1909, 1,150,000 tons in 1910 and 989,000 tons in 1911.

In Alsace (at Pechelbronn) 350,000 tons of petroleum were extracted in 1913 from wells 70 to 150 metres deep, the cost of extraction being about 32*s.* per ton of the crude product.

In the United States the capital invested in 147 petroleum refineries in 1909 amounted to £36,400,000. The output in California has almost doubled since 1908. The production of 220,200,000 barrels (of 131 kilos) in 1912 was furnished by: Oklahoma, 52,000,000; Illinois, 28,000,000; Louisiana, 10,000,000; Southern Virginia, 11,800,000; Texas, 10,500,000; Ohio, 8,500,000; Pennsylvania, 8,000,000; Indiana, 1,200,000; Kansas, 1,300,000. The output from the new borings at Caddo, near Shreveport (Louisiana) was 3358 barrels (of 150 litres) in 1906 and about 7,000,000 barrels in 1911; the borings are as much as 700 metres deep and some yield 25,000 to 70,000 barrels (density 0·815) per day.

In 1911 the United States exported 4,000,000 tons of petroleum (£12,200,000) and in 1912, 6,500,000 tons.

To transport petroleum from Baicoi to Costanza, the Roumanian Government in 1912 projected the construction of a pipe-line 300 kilometres in length, to cost £720,000. The number of companies connected with the petroleum industry was 59, but only one-half of this number were successful. The output in 1911 was furnished by: the Prahova district, 1,440,765 tons; Dambovitza, 88,971; Buzen, 68,981, and Bacau, 26,402 tons.

The Roumanian refineries treated in 1903 314,718 tons of crude petroleum, and in 1904 391,387 tons, which yielded 62,218 tons of benzine, 109,510 tons of lighting oil, 30,214 tons of mineral oils, and 173,661 tons of residues. In 1909 Roumania exported 420,000 tons of petroleum, benzine and mineral oils, while in 1910, out of a production of 1,352,300 tons, 339,300 tons of refined petroleum and 125,750 tons of benzine were exported.

In Russia the output in 1912 was 560,000,000 poods (1 pood = 36 lbs.) furnished by: Baku, 415,000,000 poods; Surachany, 31,000,000; Grosny, 65,000,000; Tscheleken, 12,000,000; Binagad, 10,000,000; Maikop, 9,000,000; Ferghana, 4,000,000; island of Swiatoi, 3,000,000, etc.

The importation into France (about 25 per cent. from Russia and 70 per cent. from the United States) is as follows (tons):

	1913	1914	1915	1916
Crude petroleum .	159,459	116,070	18,565	39,000
Refined petroleum	208,960	182,400	219,400	248,200

Almost all the petroleum produced in Italy is obtained from Montechino, that furnished by Velleia continually diminishing in amount. Up to 1907 the imports into Italy were derived to the extent of two-thirds from the United States, one-fourth from Russia, and only a little from Roumania, but after the establishment of new commercial treaties these proportions underwent marked change, Roumania alone supplying 29,000 tons in 1909. Further alterations followed readjustments in the customs' duties.

The Argentine imported petroleum to the value of £400,000 from the United States in 1909, the imports into Brazil, also from the United States, being valued at £1,320,000 in the same year.

The consumption of petroleum for lighting purposes by different countries is quite different proportionately from the production, as is shown in the following Table, which gives the mean consumption in kilos per inhabitant in 1904 and in 1911:

	Annual consumption per inhabitant.	
	1904.	1911.
United States	25·21	30
Germany	16·72	11·6
England	11·84	—
France	8·22	—
Russia (140,000,000 inhabitants)	7·51	—
Japan	6·65	—
Belgium	—	20·7
Roumania	4·50	—
Denmark	—	24·4
Austria-Hungary	4·31	—
Norway	—	23·3
Italy	2·21	—
Greece	—	1·8
India (300,000,000 inhabitants)	1·7	—
Spain	—	1·6
China (300,000,000 inhabitants)	0·85	—
Holland	—	29

The *units of measure* of petroleum in different countries have already been given on p. 65.

In view of the enormous and increasing consumption of petroleum, it may be interesting to know how much longer the known stock of petroleum in the earth will last. According to the calculations made in 1909 by the Geological Survey Office, the known deposits of petroleum would last until 1990 if the annual consumption remained at its present amount, but if the consumption increases in the same proportion as it has been doing during the last few years, the deposits will be exhausted in 1935. Account must, however, be taken of the new sources discovered every year and of the fact that many regions still remain to be explored.

The price of rectified petroleum [1] at Batoum before the war was about 7*s.* 2*d.* per quintal

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[1] **Tests for Lighting Petroleum.** A good petroleum is limpid and colourless, does not turn brown with sulphuric acid (sp. gr. 1·53), and has a specific gravity of 0·820 to 0·825 (Russian) or 0·780 to 0·805 (American); the specific gravity is determined with a hydrometer at 15° (corrected by 0·0007° for each degree of temperature) and referred to water at 4°. It should not have an acid *reaction;* when 10 c.c. of the petroleum is dissolved in a mixture of alcohol and ether previously rendered neutral to phenolphthalein, an immediate violet coloration should be produced on addition of a single drop of N/10 alcoholic caustic soda. When subjected to *fractional distillation* in the Engler flask (p. 75) it should not yield products distilling below 110°, only 5 per cent. or at most 10 per cent. up to 150°, and less than 10 per cent. or at most 15 per cent. above 330°; in the distillation products the difference in specific gravity between Russian and American petroleums is increasingly marked. American petroleum is distinguished from the Russian (*see* pp. 70 *et seq.*) also with the *refractometer* (*see later:* Oils and Fats), and by the different solubilities of the fractions of equal specific gravity in a mixture of chloroform and aqueous alcohol (Riche-Halphen test). This test is carried out as follows: Of each fraction with specific gravity higher than 0·760, 4 grams is weighed into a beaker, and from a burette a mixture in equal parts of anhydrous chloroform and 93 per cent. alcohol is run in until the turbidity first formed suddenly disappears:

Density	0·760	0·770	0·780	0·790	0·800	0·810	0·820	0·830	0·850	0·880
American petroleum (cubic centimetres solvent)	4·3	4·6	5·2	5·9	6·6	7·7	9·5	11·3	—	—
Russian petroleum (cubic centimetres solvent)	4·0	3·8	4·1	4·2	4·0	4·2	4·5	5·0	6·4	11·9

Italian petroleums behave like the Russian, but this reaction does not serve to distinguish between the other European petroleums (Utz, 1905).

The *viscosity* determined with the Engler viscometer (*see later:* Mineral Oils) should not be greater than 1·15 at 20°. The luminosity is determined with the Bunsen photometer (p. 63) and, in general, 3·5 to 5 grams are consumed per candle-hour.

The determination of the temperature at which a petroleum gives off *inflammable vapours,* (220 lbs.), and the transport to Genoa 1*s.* 5*d.*, and, making allowance for all taxes, Russian petroleum costs at Genoa 16*s.* per quintal, including the cask; the American costs 16*s.* 10*d.*, and at the present time Russian petroleum is beginning to oust the American product from the European markets. In the free port of Hamburg, Russian and American petroleums cost 16*s.* 10*d.* per quintal in 1879, 13*s.* 7*d.* in 1890, and 14*s.* 9½*d.* in 1904.

TREATMENT OF CRUDE BENZINE

The portion of crude petroleum distilling below 150° forms crude benzine, which may be separated by fractional distillation into various qualities for different commercial uses (*see* p. 75).

The *heat of evaporation* of benzines boiling up to 50° is 81·14 cals., of those boiling at 100°, 75·93 cals., and of those boiling at 130°, 71·26 cals. The *calorific value* varies from 10,500 to 11,500 cals.

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is of great importance, and in order to obtain concordant results, the Abel apparatus modified by Pensky (Figs. 93 and 94) is employed in all laboratories. The petroleum to be examined is placed in a brass receiver, *G*, up to the level-index, *h*; the cover, *D S*, carries a thermometer, *t*, which dips into the petroleum, and a clockwork mechanism, *T b*, which, when released (by a lever, *h*), opens automatically a small window in the cover; at the same instant a small oil-flame passes through the window and is immediately withdrawn, the window then closing. The petroleum receiver is surrounded by an air-chamber, *A*, which is heated to 55° in the reservoir, *W*, regulated by the thermometer t_2. For every 0·5° increase of temperature of the petroleum, the spring is released, this being continued until the flame ignites and explodes the mixed petroleum vapour and air. The slight explosion sometimes extinguishes the flame. The temperature shown at this moment by the thermometer t_1 is that of inflammability (*flash-point*), which is, however, influenced by the atmospheric pressure and should be corrected by + 0·035° for every mm. of pressure above 760 mm.

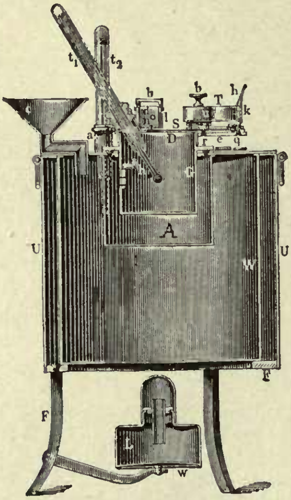

FIG. 93.

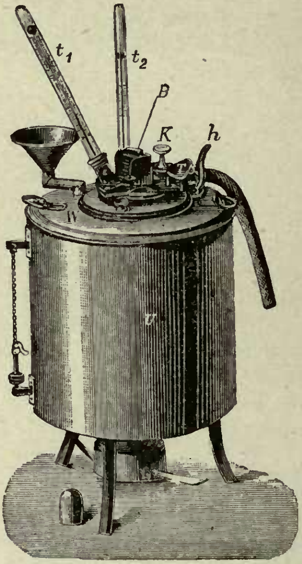

FIG. 94.

In Italy, Germany, and Austria the sale of petroleum for lighting purposes is prohibited if it shows a flash-point below 21° in the Abel apparatus; otherwise explosive vapours could be formed in ordinary lamps, even at 30° or 32°, which would be dangerous. A petroleum inflammable at above 60° (Abel) cannot be used for lamps.

A rough-and-ready test to detect if a petroleum is dangerous consists in pouring a little into a glass and throwing into it a lighted match; if the latter is extinguished, the petroleum is safe.

The *illuminating power* is determined with the Lummer and Brodhun photometer (*see* Fig. 77, p. 63). To determine the *moisture* or *water*, which does not separate well in the distillation of certain Californian petroleums, Robert and Fraser (1910) proposed adding calcium carbide and measuring the quantity of acetylene formed, this depending on the amount of water present.

The crude benzine is redistilled in small horizontal or vertical boilers, usually heated by superheated steam either in a jacket or in closed coils inside the boiler, the condensed water being collected outside the boiler.

When there are many volatile products, an apparatus similar to that used in the rectification of spirit is employed (*see* chapter on Alcohol); the heating is effected by means of iron (not copper) coils, through which steam passes, and the dephlegmation is carried out first with water and then with air. Such a system of rectifying columns is to-day in general use, and the condensation of the vapours and the cooling of the condensed benzine are effected by the crude benzine, which is thus fractionated and fuel at the same time economised.

A special apparatus for condensation and rectification, devised by Veith, consists of five iron double-walled cylinders (with water-circulation), connected in series and terminating in a sixth cylinder containing a coil with many turns for the condensation of the vapour from the preceding cylinder. The coil is cooled by ice and cold water, which then passes successively into the jackets of the other five cylinders and gradually becomes heated. These five cylinders are three-fourths full of pure iron turnings free from oil. The vapours from the boiler in which the benzine is distilled pass through cylinders 1 to 5, in each of which that part condenses which is liquefied at the temperature of the water circulating in the jacket.

The least volatile products condense in the first cylinder and the most volatile ones in the final coil. At the bottom of each cylinder is a pipe with a tap communicating with a tank.

The apparatus for distilling and rectifying benzine are so constructed that the vapour above the boiling liquid which is mixed with air is separated from the liquid, *e. g.*, by metal gauze, so that in case of fire or explosion the liquid does not ignite.

Baku petroleums give only 0·2 per cent. of benzine, and those of Grosny (Russia) about 4·5 per cent. In 1902, 341,000 tons of naphtha were distilled at Grosny, 14,000 tons of benzine (about 4 per cent.) being obtained. Pennsylvanian petroleums give up to 12 per cent. of benzine, and those from Campina (Roumania) 3 to 5 per cent.; a petroleum from Anapa (Caucasus) gave 28 per cent. Italian petroleums from Emilia yield 30 to 35 per cent. of benzine.

After the fractional distillation of the benzine the separate portions are often refined by treatment with concentrated sulphuric acid mixed with 0·2 per cent. of potassium dichromate and 0·01 per cent. of lead oxide. Fuming sulphuric acid also gives good results, but animal charcoal and magnesium hydrosilicates are not very satisfactory. The treatment is carried out in closed vessels with mechanical stirrers (the use of compressed air being inapplicable here), similar to, but smaller than, those used for refining petroleum (*see* Fig. 88, p. 78). After removal of the acid, the benzine (not stirred) is treated with a spray of water, which is then withdrawn from below. The benzine is next mixed for some minutes with 1 to 2 per cent. caustic soda solution which is decanted off, two washings with water then following. In some works a single refining of the crude benzine, prior to rectification, is preferred, counter-current apparatus in series effecting continuous refining.

The benzines obtained by destructive distillation according to the cracking process (*see* pp. 33 and 87) cannot be refined by means of sulphuric acid, since they are rich in unsaturated hydrocarbons, which give considerable heating with the acid. Such benzines are of less commercial value than ordinary benzines, to which they are added in small proportions.

Benzine is produced mainly at Baku and in Pennsylvania, but some is refined in Germany and large quantities are sent to Europe from the East Indies—from Java, Sumatra, and Borneo; Galicia and Roumania also yield large quantities.

Commercial benzines are of various qualities, and as they consist of mixtures of different hydrocarbons, they have no well-defined characters, their densities and boiling-points varying between certain limits established by commercial usage and depending on the origin of the product. Thus, American automobile benzines (petrols) have the sp. gr. 0·695 to 0·705, and the b.-pt. 60° to 100°, whilst for Indian benzines the sp. gr. is 0·705 to 0·715 and the b.-pt. 65° to 120°. It would be more rational to lay down the rule that the first drop should not distil below 60° and the last drop not above 100° (or 120° for Indian benzine), and that at 95° (105° for Indian) at least 95 per cent. should distil, and that at 100° (or 120°) not more than 1 per cent. of residue should remain.

Rational rectification of crude petroleum benzines yields the following products.

Rhigolene (*see* p. 37), used sometimes as a solvent and as an anæsthetic, has the sp. gr. 0·600 to 0·630 and the b.-pt. about 35° (more volatile products form *cymogen*), and consists mostly of pentane and isopentane. *Gasolene* has the sp. gr. 0·630 to 0·666, boils at 40° to 50°, and contains hexane and some of its isomerides; it serves to carburet the feed-air for special lamps and in some cases as a solvent. *Petroleum ether* contains pentane, hexane, and higher hydrocarbons, boils at about 50° to 60°, has the sp. gr. 0·660 to 0·670 (in Russia and America it is divided into various qualities boiling between 50° and 80°), and is soluble in twice its volume of alcohol-ether and also in chloroform and carbon disulphide; it dissolves fats, resins and rubber and is also used to carburet air; the good qualities do not colour an equal volume of sulphuric acid when shaken with it; if adulterated with tar benzene, it emits an odour of bitter almonds when shaken with a mixture of equal volumes of concentrated nitric and sulphuric acids.[1] *Benzine for removing spots* boils at 70° to 90° and has the sp. gr. 0·700 to 0·720; if too volatile, it leaves a ring on the fabric in place of the spot. *Benzine for cleaning* has the sp. gr. 0·725 to 0·730 and distils completely below 100° (otherwise it imparts an unpleasant odour to the fabric). *Solvent benzine* is used to extract fats from industrial products (wool, bones, etc.) and also alkaloids; the different qualities boil between 80° and 150° (sp. gr. 0·710 to 0·735). *American heavy engine benzine* has the sp. gr. 0·735 to 0·755, and the Indian variety, 0·750 to 0·770; the more expensive automobile benzine is sometimes adulterated with this cheaper product, especially for motor lorries. *Benzine to replace oil of turpentine* is used for paint and has a sp. gr. sometimes as high as 0·800.

The consumption of benzine in the various countries of Europe amounted in 1908 to: 115,000 tons in Germany, 130,000 tons in France, 100,000 tons in England, 10,000 tons in the Netherlands, 110,000 tons in Russia, 20,000 tons in Roumania, 10,000 tons in Austria and Galicia, and 25,000 tons in other countries. The United States produced 800,000 tons of benzine in 1908 and the Dutch Indies 260,000. In succeeding years the consumption increased enormously owing to the rapid development of motoring.[2]

The *price* of light and heavy benzines doubled between 1909 and 1914 (in Germany the light products cost £12 16*s*., and the heavy ones £8 per ton in 1909). The average consumption per kilometre may be taken as 180 grams for motor-cars and 600 grams for heavy commercial vehicles (these use also the cheaper heavy benzines).

TREATMENT OF PETROLEUM RESIDUES

A. Lubricating Oils. *B*. Vaseline. *C*. Paraffin Wax.

(*A*) **LUBRICATING OILS.** The crude petroleum residue remaining in the boilers even at 300° (astatki or masut)[3] forms a brownish black mass with a greenish reflection,

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[1] A more certain test is the very sensitive indophenine reaction, due to thiophene (*q. v.*), which is always present in benzene from tar.

[2] France imported the following amounts of petroleum benzine (especially from the United States): 170,000 tons in 1913, 172,000 in 1914, 214,000 in 1915, and 325,000 in 1916.

The output of benzine in the United States was 12,000,000 barrels (of 159 litres) in 1909, while in 1913 that for motoring alone amounted to about 17,000,000 barrels.

The quantities of crude benzine imported by Germany (one-half from the Dutch Indies and the rest from Austria, Roumania, and Russia) were: 133.813 tons in 1909 and 188,000 in 1911, the pure benzine imported being 5864 tons in 1909 and 7387 in 1910. The output in Germany was 133,765 tons in 1910, and 165,058 tons (£1,440,000) in 1911.

The Italian production and importation of benzine were as follows (tons):

	1905	1910	1912	1913	1914	1915	1916	1917
Production .	—	2,000	4,000	3,000	2,000	2,000	2,000	—
Importation .	3,000	11,000	23,000	30,000	41,000	54,000	109,000	109,000

Roumania produced 231,000 tons of benzine in 1910, and the Argentine imported benzine to the value of £344,000 in 1909.

[3] *Masut* contains, on the average, 87·5 per cent. C, 11 per cent. H, and 1·5 per cent. O; it has a mean sp. gr. of 0·91, an ignition temperature of 110°, and a calorific value of 10,700 cals. When used as a fuel it is gasified, the vapours, mixed with compressed air, burning completely; it is often burnt directly after pulverisation with compressed air or steam.

In view of the great calorific value of petroleum residues and their increasing production, new outlets have been sought for them; they should have a great future as a substitute for coal in the heating of boilers, steam-engines, ships, etc.

As has been already stated, however, this use of it is diminishing in Russia, although continually extending in the United States. In Italy attempts have been made (1911) to burn dense and sometimes semi-solid at ordinary temperature, and often with a burnt, faintly creosotic smell; it has the sp. gr. 0·900 to 0·950 and the coefficient of expansion 0·00091; that of Baku contains no paraffin wax and hence does not freeze, and gives inflammable vapour even at 120° to 160°. When these residues are discharged from the boiler, in order to cool them and so prevent them taking fire they are passed through the tubes which serves to heat the crude petroleum before introducing it into the boiler. At Baku the residues, which form almost two-thirds of the crude naphtha, are largely used as a fuel for the distillation vessels and also for locomotives and marine engines, the calorific power being 9700 to 10,800 cals. and 1 kilo being able to evaporate as much as 14 to 15 kilos of water.

Utilisation of a great part of these residues was commenced after the first American and Scotch samples (from shale oils) were exhibited at the International Exhibition at Paris in 1867. In Russia enormous quantities of residues, of almost no commercial value, accumulated every year. Their utilisation was initiated in 1873 at Balachna (near Nijni Novgorod) and later at Baku by the Ragosin process for preparing the best lubricating oils (those of Baku are highly valued) by distilling the residues by means of superheated steam, so as to avoid the formation of empyreumatic odours.[1]

The distillation of these oils, and also that of the oils transuding during the refining of paraffin wax (*see later*), is now carried out in long horizontal boilers, since in vertical ones—which were used at one time—the vapours, in contact with the heated walls, give products of profound decomposition and of bad odour. Direct-fire heating may be partly

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it, after pulverisation, directly under boilers, and it might be used advantageously if it did not cost at the factory more than about £2 8*s*. per ton, coal giving 8000 cals. costing £1 8*s*.; the cost of transport is, however, excessive, increasing the price from 8*s*. to 12*s*. at the refinery to £2 8*s*. in Italy. The Customs duty (Italy) is only 1*s*. 7*d*. per ton.

The heavy oils extracted from petroleum residues are largely used for special engines of the Diesel type.

[1] **"Cracking" Process.** In some cases it is convenient to convert the heavy mineral oils (and also the *masut*) into petroleum for lighting, use being made of the process of *cracking*. This is based on the fact, established in 1872 by Thorpe and Young, that, when the vapours of heavy petroleums are superheated, they yield gaseous hydrocarbons (6 to 8 per cent.) usually poorer in hydrogen (ethylene series) and lighter liquids which may be used as second-quality petroleum. The operation is carried out in a vertical boiler (Fig. 95), placed in a furnace so that its walls are strongly heated by the hot fumes circulating round them. The boiler is not completely filled with masut, so that the vapours evolved, coming into contact with the red-hot walls above the liquid, are decomposed; after separation in a dephlegmator of the heavy oil carried over, the vapours are progressively liquefied in ordinary condensers or refrigerators, yielding lamp oil, benzine, etc., whilst the remaining gas is used for heating or for gas-engines. A mineral oil from Ohio treated by this process gave the following products: 25 per cent. of benzine (sp. gr. 0·650 to 0·745), 33 per cent. of lighting petroleum (sp. gr. 0·800 to 0·840), 10 per cent. of light paraffin oils for burning (sp. gr. 0·854 to 0·859), 31 per cent. of solid paraffin wax and paraffin oil (sp. gr. 0·870 to 0·925), and 3 per cent. of coke and loss.

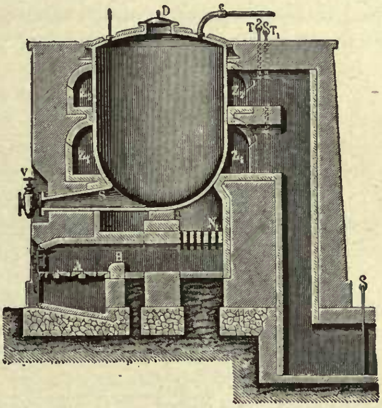

Fig. 95.

Manufacture of Benzene from Naphtha. Attempts in this direction had already been made as early as 1875, and later Ragosin and Nikiforow, Krey, Laing, Dewar, and Redwood attacked the problem, but without practical success. Recently Nikiforow appears to have succeeded, and he has devised a plant for treating 2400 tons of crude naphtha and producing 262 tons of benzene. He subjects the naphtha to two distillations under different pressures, in a retort first at 500° and then at 1000°. In this way 38 per cent. of tar containing 50 per cent. of aromatic compounds is obtained, together with an abundant supply of gas which serves for heating, lighting, and power purposes. After redistillation and rectification of the first of these products, a final yield of 12 per cent. of benzene and toluene is obtained, 3 per cent. of naphthalene, 1 per cent. of anthracene, and various secondary products. Benzene thus prepared will apparently cost £10 per ton and the aniline oil (used in dyeing) obtainable from it would cost about one-half as much as that on the market in Russia. J. Hausmann (Ger. Pat. 227,178, 1909) also obtains benzene and its derivatives by passing the vapours of mineral oil into red-hot tubes, and into contact with catalytic agents (oxides of iron, lead, and cerium, sulphate of iron, etc.).

used in conjunction with internal heating by superheated steam at 220°, and the distillation is facilitated by carrying it out in a vacuum (*see* p. 77).

Fig. 96 shows the plant used by Nobel Brothers at Baku. The condensation is effected in long, parallel, slightly slanting pipes, d, d_1, d_2 (40 to 50 cm. in diameter), communicating alternately at the ends. The first of these is cooled by air alone, the second by water, and the third by very cold water that circulates in a coil; H is an exhaust-pump. At the bottom of each of these pipes is a discharge pipe for the mineral oil condensates, which pass to water-separators; thus three qualities of oil are obtained in three separate tanks: 20 to 25 per cent. of lamp oil, sp. gr. below 0·890; 6 to 10 per cent. of spindle oil, sp. gr. 0·890 to 0·900; 25 to 30 per cent. of engine oil, sp. gr. 0·900 to 0·920; 3 to 4 per cent. of cylinder oil, sp. gr. 0·925; 3 per cent. of tar; and 5 per cent. of loss. The quantity of steam consumed varies from 100 to 150 per cent. of the amount of oil distilled and the quantity of masut treated every twenty-four hours corresponds with about double the volume of the boilers.

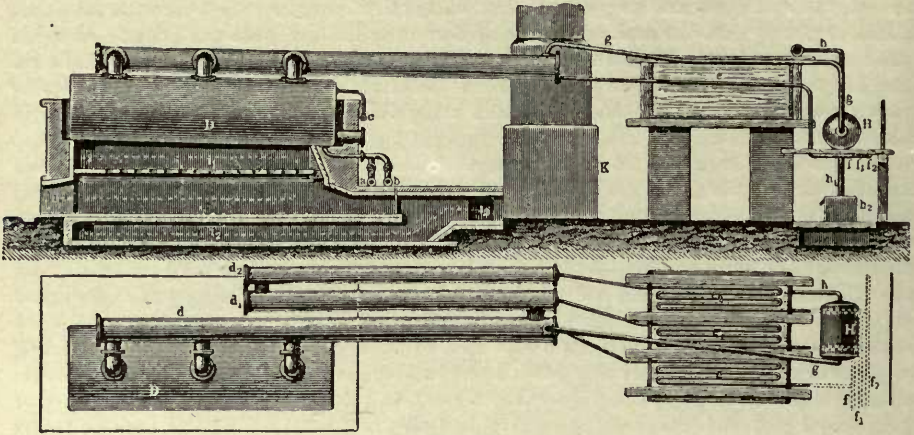

FIG. 96.

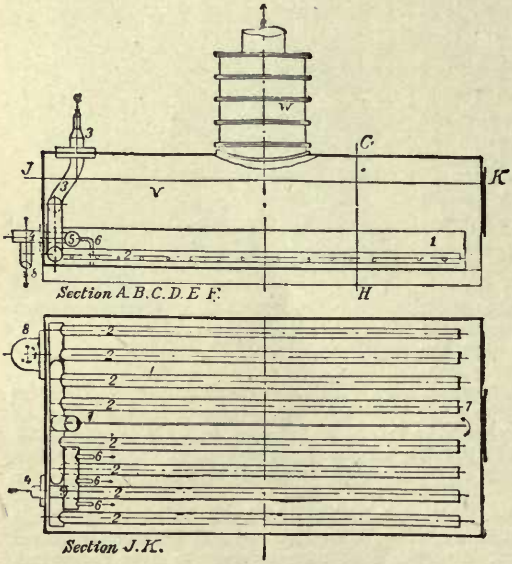

FIG. 97.

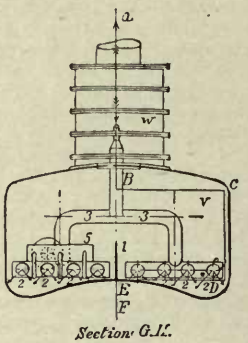

FIG. 98.

A somewhat different apparatus, which has also given good results for the *distillation of tar* and of its heavy oils, is that made by the firm of Hirzel in Leipzig. The large boiler, *BV*, with a convex base (Figs. 97 and 98) is divided longitudinally by a metal partition, 1, which allows the two halves of the boiler to communicate at the end, 7; the distillation products enter at the tube 4, connected with the horizontal pipe 5, from which the liquid descends to the bottom of the first half of the boiler along the tubes 6; the superheated steam enters by the tube 3, which is forked half-way down the boiler and connects with a battery of horizontal perforated pipes, 2, running along the bottom of the boiler. The liquid moves slowly in a comparatively thin layer from the first to the second half of the boiler, passing through the space 7, and issuing at the tube 8; the vapours are collected in the dome, *W*, containing perforated discs to condense the drops carried over with the vapours, the latter proceeding through the tube *a* to the rectification or fractional distillation apparatus. In 1911 the Hirzel apparatus was also used by a large Italian firm of metallurgical coke manufacturers and tar distillers.

All these crude mineral lubricating oils, after being freed from moisture by heating, are refined by prolonged shaking in apparatus similar to that shown in Fig. 110 with 5 to 10 per cent. of concentrated sulphuric acid (containing not more than 0·01 per cent. of nitrous acid) and, after decantation of the black acid, with 0·4 to 0·8 per cent. of a concentrated caustic soda solution (23° Bé.), just as with lamp oil, but at 60° to 65°, this being followed by washing with hot water. The largest proportions of the reagents are used with the denser, darker oils, the stirring being then effected with mechanical stirrers instead of with air. In these refining operations 3 to 5 per cent. of the mineral oil is lost during the acid treatment and 4 to 6 per cent. during the alkaline treatment. The residues in the boilers, if they are not solid coke, but pasty, are dissolved in benzene as a black varnish for iron, or are used as an adhesive in the manufacture of briquettes from coal-dust, or as a fuel.

According to Ger. Pats. 161,924 and 161,925, it is proposed to treat crude mineral oils with a saturated solution of sodium chloride and carbonate, to blow air in for some time, and finally to distil in presence of an oxide of manganese.

To render mineral oils *inodorous*, or nearly so, they are treated in the hot with formaldehyde, and, after addition of alkali or acid to the mass, a current of steam is passed through (Ger. Pat. 147,163). According to Ger. Pat. 153,585, the 20 per cent. of crude mineral oil is distilled with superheated steam at 180° in presence of 1 per cent. of aqueous lead acetate solution. The distillate is free from sulphur and forms a lighting or gas-engine oil; the residue, after filtration, forms a denser and almost odourless lubricating oil. In some cases petroleum is *deodorised* by agitating with chloride of lime and a small quantity of hydrochloric acid, decanting it, shaking with lime to fix the chlorine, and sometimes adding a little amyl acetate or essence of fennel; treatment with soda lye is also resorted to, and, better still, both for mineral oils and petroleums, with sodium peroxide.

Latterly, *mineral oils soluble in water* have acquired importance for lubricating machinery, for greasing textile fibres to be combed, and for watering the streets to prevent dust. They are prepared by the Boleg process (Ger. Pats. 122,451, 129,480, 148,168, 155,288): the mineral oil is heated in a closed vessel, fitted with a condenser, at a temperature of 60° to 70° or above by means of indirect steam; at the same time finely divided compressed air, after addition of a little caustic soda solution, is injected; a small quantity of resin soap or a sulphoricinate is subsequently introduced, the air-current being continued meanwhile, and finally the whole mass is heated under pressure in an autoclave.

Emulsions of mineral oils with water are obtained by addition of pyridine or quinoline bases or amino-acids.

To obtain from dark mineral oils less coloured oils, and in some cases oils as colourless as water (*e. g.*, *vaseline oils*), the oil is passed slowly at 30° to 50° through a series of tall, communicating cylinders, sometimes kept hot by means of steam jackets (batteries of tubes arranged in a system similar to the diffusors used for extracting sugar from beets: *see* chapter on Sugar), and charged with layers of decolorising clay separated by perforated discs or gauze to prevent the mass from becoming too compact and thus hindering the permeation of the oil. These clays are found more especially in North America, but occur also in Great Britain and, in inferior quality, in other countries; they are similar to fuller's earth, but the best is Florida earth, consisting of aluminium and magnesium hydrosilicates (*see* Vol. I., p. 738), previously subjected to slight roasting. The mineral oil remaining in the filters is recovered by displacing it by heavy tar oil (very cheap) and displacing the latter with water.

The exhausted fuller's earth may be regenerated by extracting the oil it contains by means of benzine; the latter is recovered by distillation, and that remaining in the earth by a current of steam. After this treatment the fuller's earth is heated in a revolving, cylindrical metal cylinder (like that used for cement; *see* Vol. I., p. 760), cooling being effected in a lower, revolving cylinder sprayed with water. With each repetition of this treatment, the earth loses in decolorising power.

Decolorisation is also effected by bone-black or, best of all, by residues from the manufacture of potassium ferrocyanide, which exhibit very great decolorising power (50 per cent. more than American clay); owing, however, to the new methods of manufacturing ferrocyanide, these residues are becoming scarcer and more expensive (they contain 30 to 40 per cent. of animal charcoal, considerable quantities of silica and silicates, and a little ferric oxide). The darker mineral oils are partly decolorised with sulphuric acid, sometimes together with dichromate.[1] In the case of certain dark mineral oils, repeated filtration through fuller's earth is replaced by purification with sulphuric acid and soda, but this occasions greater losses.

Carts are often greased with the so-called *consistent fats* obtained by mixing 15 to 23 per cent. of calcium soaps and mineral oils with 1 to 4 per cent. of water (if there is no water the mass remains liquid, and if there is not a little free fatty acid emulsification ceases after a time and the calcium soap separates).

REQUIREMENTS IN AND ANALYSIS OF LUBRICATING OILS. Lubricating oils serve to diminish the friction between metal surfaces in motion; by adhering strongly, although in very thin layers, to these surfaces they prevent contact between them and hence friction and heating, without sensible increase of the resistance owing to the internal friction of the oil. Lubrication is due partly to chemical phenomena (formation of metallic soaps) but more especially to physical phenomena not well understood.

Liquids which moisten surfaces (unlike mercury) exhibit great adhesive or capillary force and penetrate into the finest cracks. This capillary force (external friction) for thin layers of oil increases with diminution of the radius of curvature, and is sufficiently great to prevent direct contact of two surfaces between which the liquid is interposed, no matter how great the pressure. Thus, the resistance between the bearing and the revolving shaft it supports depends *almost* exclusively on the internal friction of the lubricating oil, *i. e.*, on the *viscosity* of the oil.[2] Of two oils with equal viscosities, the preference is naturally

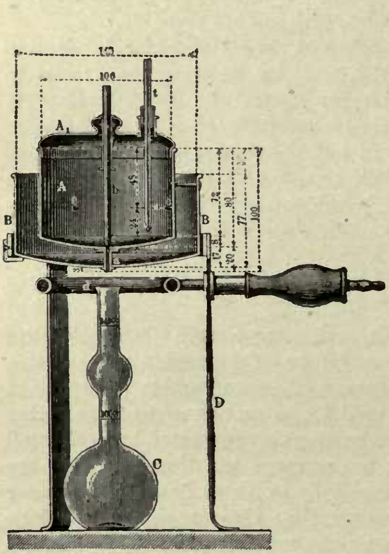

FIG. 99.

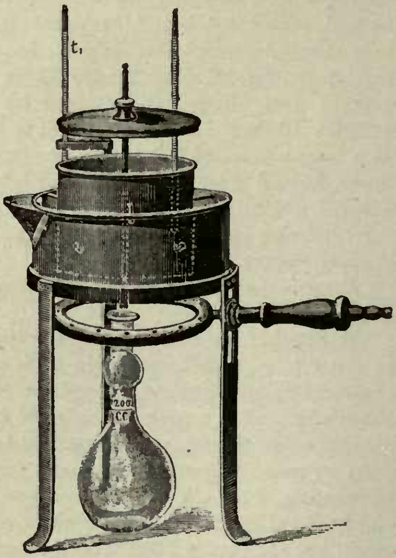

FIG. 100.

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[1] For the thorough decolorisation of *vaseline oil* the following operations are carried out: (1) Drying or dehydration; (2) treatment with 10 to 15 per cent. of fuming sulphuric acid and separation of the tarry matters formed; (3) neutralisation with caustic soda solution (10° to 12° Bé.); (4) separation of the alkali and washing with water; (5) clarification with 4 to 5 per cent. of pure 50 per cent. alcohol and removal of the milky layer deposited; (6) bleaching with dry fuller's earth and subsequent filtration.

[2] For lubricating oils it is important to determine the *viscosity* (due especially to polynaphthenes), and this is usually effected by means of the Engler *viscometer* (Figs. 99 and 100), formed

given to the one containing the smaller proportion of substances liable to undergo change (asphalte, resin, soaps, etc.). Even the best lubricating oils, when in use, are subject to more or less marked alteration (oxidation, pulverisation, emulsification, etc.), which is evident especially in ring lubrication or in the lubrication of turbines, where the oil is changed at infrequent intervals; in such cases, oils of the highest quality should be used, as replacement is expensive (some oil-boxes contain 100 to 200 kilos of oil). More rapid is the alteration of lubricants used for engines or steam-cylinders, where the temperature is 150° to 200° or even 250°, part of the oil undergoing decomposition with separation of small particles of coke and asphalte. In these cases it is important to determine the *flash-point* of the oil [1] (so that danger of ignition of the oil may be avoided); use may also be made of the *formolite reaction* and of the reaction with fuming acid (*see* p. 71). In general, where there is much pressure the viscous oils are suitable, and in other places liquid oils, although in practice mixtures of these two kinds are advantageously employed. Oil for lubricating steam cylinders at high temperatures should be resistant to great heat and to the mechanical and chemical action of steam, and should not give inflammable products at a lower temperature than 220°, or 300° where superheated steam is employed; it should possess great adhesive power and viscosity and should not contain

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of a brass vessel, *A* (sometimes gilt inside), provided with a cover, A_1, through which passes the thermometer, *t*; at the bottom of the vessel is a platinum tube, *a*, 20 mm. long and of such dimensions that it allows of the efflux of 200 c.c. of distilled water at 20° in 52 to 54 secs.; the aperture can be closed from above by the hard wooden peg, *b*. The vessel, *A*, is contained in a larger one, *B*, and the space between the two is filled with water maintained constantly at the desired temperature by means of the ring-burner, *d*, and the thermometer, t_1. The dimensions of the apparatus are exactly defined and are shown in millimetres in the figure. The mineral oil is introduced into *A* (clean and dry) up to the level indicated by the three points (about 240 c.c.). When the temperature of the oil in *A* has the desired constant value, the flask *C* is placed under the efflux tube and the peg rapidly removed, the exact number of seconds taken to fill the flask to the 200 c.c. mark being determined by a chronometer. The time required, in seconds, divided by the corresponding number of seconds for water at the same temperature gives directly the *degree of viscosity*.

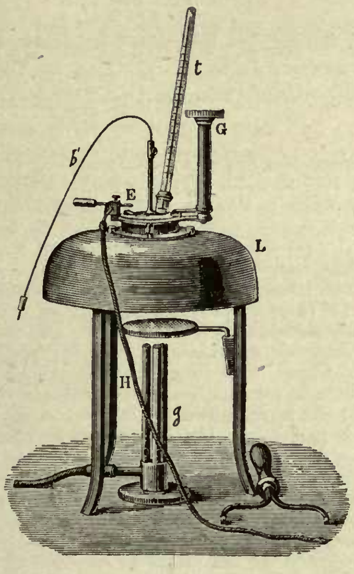

Fig. 101.

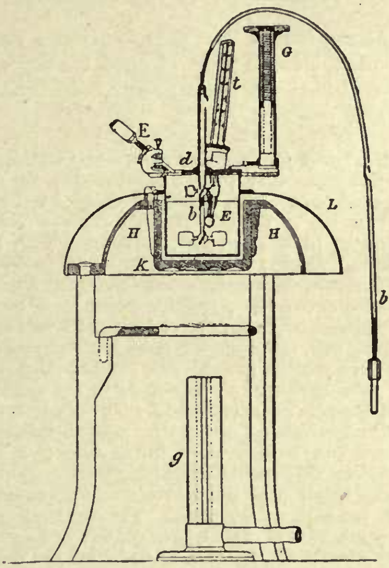

Fig. 102.

[1] The *flash-point* is determined by the Pensky-Martens apparatus (Figs. 101 and 102), which is analogous to the Abel apparatus (p. 84), but without the water-bath, being furnished instead with a stirrer with vanes, *b*, moved by twisting the metal cord, *b'*, between the fingers; it works similarly to the Abel apparatus, and the small flame, *E*, applied automatically, is fed by a small gas tube, *H*, and is relighted, every time it is extinguished, by another flame by its side. The thermometer, *t*, is graduated from 80° to 320°, and the heating is effected by the triple gas-burner, *g*, so that the temperature rises 5° per minute; observations are made by releasing the spring, at first for every 2° and later for every 1° rise of temperature.

resinous or tarry residues. No oil resists the action of steam at above 350°. The good qualities, which are more or less dark, are transparent in the liquid state. The selection for steam cylinders of oils viscous at ordinary temperatures is unimportant, as they become as liquid as water when hot; this is seen from a comparison of the following two mineral oils, the numbers giving the viscosity in seconds required for the passage of 200 c.c. of oil through the Engler viscometer (*see above*).

	at 70°	at 100°	at 150°	at 170°
Viscosity of sample I	270	116	74	67
„ „ II	835	226	93	73

The Russian engine oils are more viscous than the American, but the American cylinder oils are more viscous than the Russian. American oils with sp. gr. 0·908 to 0·920 and 0·844 to 0·899 have viscosities almost the same as those of the Russian oils with sp. gr. 0·893 to 0·900 and 0·900 to 0·923 respectively.

The specific gravities of certain American and Russian oils are as follows:

	American	Russian
Axle oil	0·908–0·911	0·893–0·895
Pale engine oil . . .	0·920	0·903–0·905
Dark engine oil . . .	0·884	0·900–0·920
Cylinder oil . . .	0·886–0·899	0·911–0·923

At the foot of the page is given a summary of the criteria laid down by Holde for various lubricating oils of good quality and the requirements to be answered by those supplied to the Italian railways.[1] In Russia special oils of more than thirty different types are now prepared.

[1] (1) *Oils for spinning spindles.* Clear liquids, viscosity (*see* Engler viscometer), 5 to 12 at 20°, inflammability (in the Martens-Pensky apparatus), 160° to 200°. (2) *Oils for ice-machines or compressors.* Very fluid; viscosity, 5 to 7 at 20°; freezing-point below — 20°; inflammability, 140° to 180°. (3) *Oils for light engines and transmission, motors, dynamos.* Medium fluidity, viscosity, 13 to 25 at 20°; inflammability, 160° to 210°. (4) *Oils for heavy engines and transmission.* Dense; viscosity, 25 to 45 to 60 at 20°; inflammability, 160° to 210°. (5) *Dark oils for locomotives and railway carriages.* Viscosity, 45 to 60 (summer), 25 to 45 (winter); inflammability above 140°; freezing-point, — 5° (summer), — 15° (winter). (6) *Oils for steam cylinders.* Very dense or buttery; viscosity, 23 to 45 at 50°; inflammability, 220° to 315°. For these buttery oils, the *dropping-point* is determined by the *Ubbelohde apparatus* (p. 6). (7) *Oils for explosion engines* (motor-cars, etc.) are somewhat different from those for steam cylinders, since the gases igniting and exploding in the cylinder of an internal combustion engine generate very high temperatures (1200° to 1400°), and these, added to the rapid motion of the piston, result in the combustion of part of the lubricating oil, which passes into the exhaust gases. Such combustion is the more incomplete (and hence gives strong-smelling products instead of inodorous CO_2 and H_2O), the higher the proportion of dense, high-boiling point products present in this fraction of the lubricant. Consequently oils for this purpose should not be too dense or of too high a flash-point. The combustion of these compounds is the more complete, the less the proportion of carbon they contain and hence the less oxygen they require for their combustion, since almost all the air drawn in by the engine is necessary for the complete combustion or explosion of the combustible mixture working the engine and insufficient oxygen to burn completely the part of the lubricant referred to results in the separation of carbonaceous substances which foul the cylinder and cause it to work irregularly, while the exhaust gases assume a bluish colour and an unpleasant odour. The addition of vegetable and animal fatty oils also produces these inconveniences. F. Schwarz and H. Schlüter (1911) found that, if the lubricating oil is shaken with acetone, the latter dissolves and removes mostly the denser products of high boiling-point, whilst the insoluble portion is more fluid, and usually forms an oil which burns completely in internal combustion engines without carbonising or giving a disagreeable smell. In general good oils for this purpose are pale and have a viscosity of 6 to 13 at 50° (or 25 to 65 at 20°); they contain little paraffin wax, so that they do not freeze readily in winter and thus do not obstruct the feed-pipes.

The authorities of the Italian railways demand Russian oils, since these freeze only below — 10°, whilst the American ones solidify at 0°; they must not contain water, that is, they must not froth if heated to 129°; they must give no deposit even after standing for forty-eight hours; the viscosity must be at least eight times that of water; they should be perfectly neutral and should not contain shale oil, resin oil, animal or vegetable oil, or tar oil, as these lower the quality; they should not have the slightest "drying" properties in the air (smeared on glass), or have a density below 0·91 or a flash-point below 150° to 180°; they must not contain more than 10 per cent. of light oils distilling below 310°; when shaken with water, the oil should separate immediately without the water remaining whitish.

With *mineral oils for automobiles* it is important to test for *resin oils*, the procedure being as

Mineral oils are also used in special engines to utilise their high calorific value (10,500 to 11,700 cals.). Scherman and Kropf (1908) found that the *calorific power* of mineral oils and, to some extent, that of petroleums is inversely proportional to their specific gravity. Mineral oils are often used as insulators in electric motors.

The origin and properties of certain mineral oils are often related to their content of paraffin wax, the determination of which is effected as described above.

The *acidity* is determined by titrating 50 c.c. of the 100 c.c. of 50 per cent. alcohol (neutralised) shaken up with 10 grams of the mineral oil; expressed as SO_3, it should be below 0·01 per cent.

It is sometimes useful to know if certain more or less dark mineral oils are true refined products obtained by the distillation of petroleum residues (masut, etc.), or if they are merely the crude residues themselves diluted with more or less mineral oil. Charitschkoff (1907) found that the rise of temperature on mixing with concentrated sulphuric acid (*Maumené number: see also* chapter on Fats) in a Beckmann apparatus (*see* Molecular Weights, Vol. I.) is 2·2° to 3·5° for all distilled products (lamp oil and various lubricating oils) and 4° to 8·5° for all non-distilled products (crude naphtha, masut, etc.). In certain cases the formolite reaction and that with nitric acid (*see* pp. 71, 91) give reliable indications.

STATISTICS. In all countries the consumption of mineral oils is continually increasing.

The United States produced 11,000,000 barrels of mineral oils in 1909 and exported 5,000,000 barrels in 1910 and 5,600,000 in 1911.

France imported 144,600 tons of mineral oils in 1913, 101,170 in 1914, 106,610 in 1915, and 170,014 in 1916, and exported 7937 tons in 1913, 6579 in 1914, and 4665 in 1915.

Germany imported 216,987 tons in 1909, 236,516 in 1910, and 260,242 in 1911, and produced 85,850 tons in 1910, and 93,889 tons (£680,000) in 1911. Before the war the price was £8 to £12 per ton, during the war it rose to £160, and the Bavarian railways lubricated their wagons with coal-tar oils suitably prepared.

In 1909 the Argentine imported mineral oils to the value of £500,000, while the imports into Brazil were valued at £280,000 in the same year.

The imports into Italy were: 29,250 tons in 1905, 40,467 in 1908, 49,181 in 1910, 60,311 in 1912, 58,098 in 1913, 60,874 in 1914, 80,020 in 1915, 67,699 in 1916, and 75,764 in 1919.

(*B*) **VASELINE** (or *mineral fat*). This was prepared for the first time by Cheeseborough in 1871 and forms a white, buttery mass constituted almost exclusively of various high, saturated hydrocarbons.

It is prepared, especially in America, by heating certain pale, crude, Pennsylvanian petroleums by direct fire in open boilers, and passing into the mass a current of hot air until the desired consistency or sp. gr. (0·86 to 0·87) is reached. The mass is then decolorised by passing it, while still hot, repeatedly through animal charcoal or other decolorising agents (*see* p. 89). It is also prepared from the residues of Galician and German petroleum by diluting them with benzine and repeatedly refining with concentrated sulphuric acid. It melts at 33° to 40°.

Artificial vaselines are also placed on the market, these being obtained by dissolving paraffin wax or cerasin (*see later*) in paraffin oil; they may be distinguished from the natural vaselines, the latter being sticky and ropy and the former not. At 60° the viscosity (Engler) of the natural vaselines is 4·5 to 7·5, and that of the artificial ones little more than 1; the latter contain 11 to 35 per cent. and the natural vaselines 63 to 80 per cent. of paraffin wax, insoluble in 98 per cent. alcohol at 0°. The natural vaseline after solution in ether and precipitation with alcohol forms a sticky mass and the liquid remains turbid; the artificial variety, on the other hand, is precipitated in flocks and the liquid is left clear.

Gelatinised vaseline oil, also prepared nowadays, is transparent and does not deposit paraffin wax, even if added in considerable quantity; it is obtained by heating vaseline

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follows: 5 grams of the oil are heated with 25 grams of 60 per cent. alcohol to 40° to 50° on a water-bath, the mixture being well shaken until it emulsifies, allowed to cool and filtered. The alcohol is driven off from the filtrate on a water-bath and the cold residue treated, drop by drop, with 2 to 3 c.c. of dimethyl sulphate: if resin oil is present, a red coloration is produced.

oil (sometimes with a little sulphuric acid) at about 200° and adding, at a certain moment, a small quantity of soap.

For the decolorisation of vaseline and vaseline oil *see above.*

Vaseline is used in pharmacy for the preparation of unguent medicines, also for the preparation of lubricants, and, in large quantities, for coating metallic articles to preserve them from rusting and oxidation; it is also used in the manufacture of smokeless powder.

Italy imported the following amounts of vaseline:

		1908	1910	1912	1913	1914	1915	1916	1917	1918
Natural vaseline	Tons	34·8	21·7	42·3	45·2	33	99	106·9	327·6	189·5
	Value, £	2088	—	2538	—	1848	—	6842	—	26520
Artificial vaseline	Tons	75·7	88·1	81·6	64·2	51·2	16·6	181·1	43·4	151·7
	Value, £	2483	—	2546	—	1638	—	7968	—	18200

In 1910 Germany produced 5292 tons of vaseline of the value £36,000. France imported 173 tons in 1913, 73 in 1914, 935 in 1915, and 828 in 1916, and exported 107 tons in 1913 and 156 in 1916.

(*C*) **PARAFFIN WAX.** This was first found in petroleum by Fuchs in 1809, and Reichenbach obtained it from wood-tar in 1830, and showed its great importance as an illuminant.

Hard paraffin wax melts at 54° to 60°, has sp. gr. 0·898 to 0·915, and forms a white, translucent mass used for the manufacture of paraffin candles; it is soluble in ether (1·95 per cent.), petroleum benzine (11·7 per cent.), carbon disulphide (13 per cent.), turpentine (6 per cent.), toluene (3·9 per cent.), chloroform (2·4 per cent.) or benzene (2 per cent.), and to slight extents in alcohol (0·22 per cent.), acetic acid (0·06 per cent.), acetone (0·26 per cent.), or acetic anhydride (0·025 per cent.). By fractional distillation of paraffin wax in a vacuum Mabery (1912) isolated tricosane (*see* Table, p. 32), tetracosane, pentacosane, hexacosane, octocosane, and nonocosane (m.-pt. 62° to 63°).

Soft paraffin wax with m.-pt. 42° to 48° and sp. gr. 0·88 to 0·89 is used as an adjunct in wax and stearine candles, to impregnate wooden matches, in dressing textiles, and as a preventive of frothing during the concentration of saccharine juices (*see* Sugar); it serves also as an insulator of electrical conductors and as a cold bath in the manufacture of *hardened glass*.

Most of the *paraffin wax* and *paraffin wax oil* is obtained from *ozokerite* (*see later*), the tar distilled from the bituminous lignites of Saxony and Thuringia (*pyropissite*) and from the bituminous shales of Scotland and Australia, and also from boghead coal and from the residues of American and Austrian petroleum.[1]

I. PARAFFIN WAX FROM PETROLEUM RESIDUES. For this purpose an apparatus consisting of three vertical concentric cylinders is used; in the inner and outer ones circulates a non-solidifying brine, which has a temperature of — 20° and serves to separate the paraffin wax from the mineral oil in the middle cylinder (*see also* p. 78). According to Tanne and Oberländer, Ger. Pats. 226,136 and 227,334, paraffin wax is obtained from petroleum and tar residues by dissolving them in hot benzine and glacial acetic acid; on cooling, the solutions deposit paraffin wax, cerasin, or ozokerite; *see also* Process of Miss Az). To free the flakes of paraffin wax from the adhering oil the cold mass is pressed in filter-presses (up to 15 atmos.) and the cakes thus formed are finally squeezed in hydraulic presses, as is done in the case of stearine (*see this*); the blocks of wax are then spread out in a warm chamber, where the last traces of coloured oils flow away. In the Weiser process the hydraulic presses are replaced advantageously by filtering tubes wound round with-

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[1] There is also at Messel, near Darmstadt, a special layer of very soft and moist bituminous coal, consisting of clay and lignite, its bitumen, like that of the shales, being insoluble in the ordinary solvents. This coal contains 45 per cent. of water and 30 per cent. of ash, and on distillation yields 6 to 7 per cent. of tar and 6 per cent. of gas (*see* p. 103).

linen; the paraffin wax from the filter-press is broken up and forced into these tubes, being afterwards removed by steam and sent to the sweating chamber. The sweated oils are refined to prepare lubricating mineral oils (*see* p. 76).

The sweated paraffin wax is *refined* by means of sulphuric acid and decolorising agents, in the same way as cerasin is refined. If the petroleum oils are distilled in a vacuum, mineral oils are obtained which give a greater yield of paraffin wax. According to Tanne and Oberländer (Ger. Pat. 238,489, 1911), treatment of mineral oil residues or lignite tars with 10 to 20 per cent. of carbon tetrachloride readily gives paraffin wax or cerasin in good yields.

II. PARAFFIN WAX FROM LIGNITE TAR AND FROM PYROPISSITE. This special lignite, *pyropissite,* now almost exhausted, is obtained from deposits of oily and resinous woods which, according to Potonié and Heinhold, underwent fossilisation during the tertiary epoch. It is extracted moist (up to 55 per cent. of water) from the mines in Saxony and Thuringia, especially in the neighbourhood of Halle a/S., where the deposits are 35 to 40 metres below the surface and have a thickness of 2 to 5 metres over an area of about a square kilometre. It forms a blackish-brown, more or less plastic mass, greasy to the touch, and when dry is yellowish-brown, friable and easy to burn; its sp. gr. is 0·9 to 1·1. In the dry state it gives up to alcohol 20 per cent. of its weight of a substance, m.-pt. 75° to 86°, giving paraffin oil on distillation.[1] The rational industrial distillation of these more or less fatty lignites or of the corresponding bitumens was commenced in Saxony and Thuringia after 1858 by C. A. Riebeck (after unsuccessful attempts to carry out the distillation in the usual way, no matter what the type of the lignite) and improved later by Wernecke.

The distillation of the broken lignite is carried out in large vertical refractory (chamotte) retorts, 8 metres high and 2 metres wide, placed in a suitable furnace so that the external walls are heated by rational circulation of the hot gases. Inside the retort are arranged conical, cast-iron rings superposed one on the other with a certain distance between, their diameter being 12 to 20 cm. less than that of the retort (*see* Figure of a similar apparatus used for the distillation of sawdust: chapter on Acetic Acid). The lignite,[2] with not

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[1] E. Erdmann gives the following results of analysis and distillation, referred to 100 parts of dry matter (the moisture is 33 to 35 per cent.):

	C	H	O	S (volatile)	Ash	Tar	Coke	Gas
Pyropissite . .	71·12	11·63	9·43	0·10	7·72	65	20	15
Bituminous lignite .	64·83	7·62	19·18	0·48	7·89	38	42	20

The sulphur content of bituminous lignites never exceeds 2 per cent.

The distillation products of these lignites consist, to the extent of 40 to 50 per cent., of slightly alkaline water (2° to 3° Bé. with 0·03 to 0·07 per cent. NH_3) from which it does not pay to recover the ammonia, and which are used only for the direct irrigation of the soil adjacent to the works; they sometimes form a troublesome waste product, which must be treated and filtered before running into rivers, or they may be poured on to the ash-heap.

One ton of bituminous lignite yields 130 to 140 cu. metres of gas containing: 10 to 20 per cent. of CO_2, 0·13 per cent. of O, 1 to 2 per cent. of heavy hydrocarbons, 5 to 15 per cent. of CO, 10 to 25 per cent. of CH_4, 10 to 30 per cent. of H, 10 to 30 per cent. of N, and 1 to 3 per cent. of H_2S. The gas has a calorific value of more than 3000 cals. per cubic metre and, after removal of the H_2S, serves for use in gas-engines, 1 to 1·5 cu. metres being consumed per H.P.-hour (one retort deals with about 3 tons of the lignite in twenty-four hours, producing about 400 cu. metres of gas). The gas is freed from ammonia by washing with water.

After quenching, the coke remaining from the distillation contains about 20 per cent. of water and volatile products, 20 per cent. of ash, and 60 per cent. of carbon. When dry, its calorific value is about 6000 cals. and, with many works, the profits are made by the sale of the coke.

[2] Now that the deposits of *pyropissite* are almost exhausted and the paraffin wax industry of Saxony and Thuringia has been subjected to the competition, first, of ozokerite (after 1870), and then (after 1880) to the more serious one of the American paraffin wax extracted from Ohio petroleums—which has invaded all the markets of the world—it has been recently discovered that when pyropissite is distilled a great part of the paraffin wax is destroyed, much better yields being obtained by extracting direct with suitable solvents (benzine, toluene, alcohol, carbon disulphide, carbon tetrachloride, acetone, etc.), which, after evaporation, leave a waxy mass; when this is purified with fuming sulphuric acid, it yields an almost white product of great value—*montan wax* (Bergwachs), similar to *cerasin* (mineral wax). The remedy for the paraffin wax crisis of Saxony and Thuringia has arrived too late, since the valuable wax has been squandered by distillation. Other layers of lignite from the region of Halle a/S. are being worked to-day, and these are extracted in the hot with benzine; the solution of bitumen extracted is first purified by thorough cooling, the paraffins being thus separated while the resins

less than 30 per cent. and not more than 60 per cent. of water, is charged in lumps at the top and descends gradually in the free annular space between the walls of the retort and the edges of the rings. When it reaches the bottom it consists of nothing but coke, which is discharged occasionally, fresh lignite being introduced at the top; the gaseous products are evolved at 140° to 150° by a large tube at the top, and the liquid products (tar) flow down the walls of the rings and are collected by a lower tube. The retorts are maintained at a dull red heat.

From a cone at the bottom the coke is discharged every hour at a temperature of 400° and is quenched with water. The vapours emitted are drawn off and gradually condensed in apparatus consisting of superposed iron tubes with a cooling surface of 80 to 100 square metres enclosed in a casing. The gases which do not condense are led under the hearth to heat the furnace, fuel being thus saved; formerly 5 to 6 tons of inferior coal were used per 10 tons of lignite distilled, but later only 1 to 1·2 tons were necessary, less labour being required (one workman per twenty furnaces) and the yield per furnace being increased (by more than 25 per cent.). The gases passing from the hearth round the furnace and retorts have a temperature of 500° to 700°.[1] Batteries of 10 to 12 retorts for each condensation unit are employed. In each furnace 3·5 to 4 tons of lignite in pieces the size of walnuts are distilled in twenty-four hours. The lignites now distilled give only 4 to 8 per cent. of tar.

Lignite tar is brownish yellow to black in colour, has a peculiar odour, and liquefies between 25° and 30°, giving a greenish fluorescence. Its specific gravity is 0·850 to 0·910 at 44°. It has an alkaline reaction (from ammonia, ethylamine, etc.) and contains about 20 to 25 per cent. of paraffin wax [2]; it distils between 80° and 400°, the bulk between 250° and 350°, and has an unpleasant odour, sometimes of hydrogen sulphide. The best lignites give the less dense tars. According to the nature of the tar (which is previously washed with acid and water [3]) the paraffin wax is obtained from it in the following ways (*see also* Part III, Distillation of Tar):

(these are recovered by evaporation of the solvent; they melt at 50° to 60° and form 15 to 25 per cent. of the crude bitumen) remain in solution. The bitumen separated in the cold is redissolved in benzine and treated with concentrated sulphuric acid, the mass being kept mixed and slowly heated to boiling. Animal charcoal is added and the liquid filtered, passed over fuller's earth (*see* p. 89), and neutralised by passing in a little gaseous ammonia. After distillation of the solvent there remains a yellowish or almost white paraffin wax melting at 82° to 85° (Ger. Pat. 216,281, 1907).

[1] For every quality of lignite and every type of furnace preliminary trials should be made to ascertain the most suitable temperature for obtaining the proper decomposition of the bitumen so as to form a tar poor in benzene and its homologues, naphthalene, etc. (produced by an excessively high temperature, although absence of these substances indicates too low a distillation temperature, the high condensed products of the methane series then containing unaltered bitumen and the gases some proportion of ethylene and acetylene; when the temperature is too high, the gases contain hydrogen and light hydrocarbons). Distillation in steam affords no advantage, since much unchanged bitumen then occurs with the tar and no ammoniacal liquor is then obtained; such liquor is, however, formed in abundance when Scotch shales are steam-distilled.

[2] In these lignite tars and bitumens Krämer and Spiller (1902) found an ester and the corresponding monobasic acid, but no glycerides or polybasic acids. Hübner (1908) found two ketones, $C_{16}H_{32}O$ and $C_{12}H_{24}O$, and a humic acid containing 8·39 per cent. of sulphur, although other investigators found only 5 per cent. and 1·7 per cent. of sulphur.

[3] The purification of lignite tars and their distillation products is effected by means of acid and alkali. In the first treatment with acid, use is made of 0·25 to 0·5 per cent. of sulphuric acid of 50° Bé., which removes traces of water and part of the basic products (pyridine). The second treatment with 3 to 5 per cent. of sulphuric acid of 66° Bé. (in two portions) serves for the removal of all the residual basic products and part of the unsaturated hydrocarbons, which otherwise would undergo oxidation and resinification, and would impart a dark colour to the oils; the sulphuric acid also causes slight oxidation (rendered evident by the marked odour of SO_2) as well as polymerisation and substitution. The action of the acid takes place in the cold, except with the tar itself and with the crude paraffin wax, which require heat. The pitch and resin formed on treatment with sulphuric acid are insoluble and are deposited on the walls of the vessel. After a rest of three hours, the acid is separated by decantation and the residue washed twice with water (perhaps with a little added calcium hydroxide) to eliminate the last traces of acid, and then treated with 4 to 6 per cent. of pure caustic soda solution (38° to 40° Be.). Treatment with alkali is applied, not to the tar itself, but only to its distillation products, a small amount of the alkali (or recovered alkali solution) being first used and then the bulk of the alkali; the so-called creosotes (which consist of phenol and its homologues and impart a bad colour and smell to the oil) are thus removed—after a stand of three hours. The alkali treatment should not precede that with acid, since there are products soluble in both alkali and acid and it is more economical to eliminate the bulk of these by means of sulphuric acid and those

(1) To the lignite bitumen or tar to be distilled, 0·2 to 0·5 per cent. of slaked lime or of solid caustic soda is added to fix the hydrogen sulphide and part of the creosote. The distillation is continued until only a solid residue of coke remains. With 2·5 tons of tar the distillation occupies about ten hours, about 0·6 ton of small coal and 0·05 ton of lignite being consumed. One workman suffices to control the distillation in ten stills and another to supervise the condensation plant. It is possible also to distil in a vacuum, the degree of evacuation being low at the beginning. Sometimes distillation at ordinary pressure in a slow current of steam (maybe superheated) is preferred. Use is nowadays made of Wernecke's continuous apparatus (*see* Part III: chapter on Tar). When the price of paraffin oils is too low, light illuminating oils, etc. (*see* note, pp. 75, 76 : Benzine from Naphtha) may be obtained by distilling them under pressure.

With very dense tars, in order to separate the creosote and certain resinous substances more efficiently, vacuum distillation in large direct-fired boilers is resorted to. This yields 25 to 50 per cent. of fatty oils, 50 to 65 per cent. of crude paraffin wax, and 7 to 9 per cent. of coke, which is burnt, together with the gases from the distillation, to heat the boilers. The mass of crude paraffin wax is purified with acid and alkali, or with acid and subsequent distillation. The more solid part is then separated from the oily part by cooling the mass in vessels holding 100 to 200 kilos, around which circulates a very cold solution (the non-solidifying liquids used for ice-machines, *see* Vol. I., pp. 261, 621). When the oily or buttery part (which is distilled for the extraction of solar oil and second-grade paraffin) is separated by filtration from the crystallised paraffin wax, the cakes of the latter are pressed in hydraulic presses at 150 atmos. to remove the 20 per cent. of oil still contained in them. The solid cakes which remain are yellowish in colour, and are purified by melting them several times with 10 to 15 per cent. of benzine and pressing them at 200 atmos. in a hydraulic press. To get rid of the smell of benzine the paraffin wax is heated in iron cylinders with high-pressure steam, the hot wax being then passed through the decolorising material [animal charcoal, ferrocyanide residues, or magnesium hydrosilicate clay (*see* p. 89)]. The small quantity of this material retained by the paraffin wax is finally removed by filtration through paper, the wax being then allowed to solidify in large shallow moulds.

Miss Az has recently suggested the purification of crude paraffin wax by treating it either fused or as powder, between 60° and 70°, with a solvent (methyl or ethyl alcohol, acetone, or acetic acid or anhydride). The paraffin wax is insoluble and the impurities soluble in these solvents. Paraffin wax thus purified appears to be of better quality than that purified in the ordinary way (*see above* : Weiser's process).

The tar is sometimes distilled above a certain temperature with superheated steam;

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remaining, which are less soluble and more easily removable, by means of soda; with this procedure less secondary decomposition occurs.

The acid treatment is carried out in cylindrical wrought-iron tanks with conical bases lined with pure lead 4 mm. thick, the mass being stirred for about half-an-hour by a stream of air.

Tars free from bitumen are best treated with 0·25 per cent. of sulphuric acid of 50° Bé., then with 3 to 4 per cent. of acid of 66° Bé., and finally with hot water containing a little milk of lime, formation of emulsions being avoided by thorough agitation. Distillation of the tar then gives paler products, a higher yield of paraffin wax and less loss of gas, etc. If the tar contains bitumen, or if vacuum distillation is employed, such preliminary treatment with sulphuric acid is inadvisable.

The blue fluorescence shown by some of these distillation oils is removed by shaking them with 0·25 to 0·5 per cent. of nitronaphthalene, which separates on standing and is then decanted off.

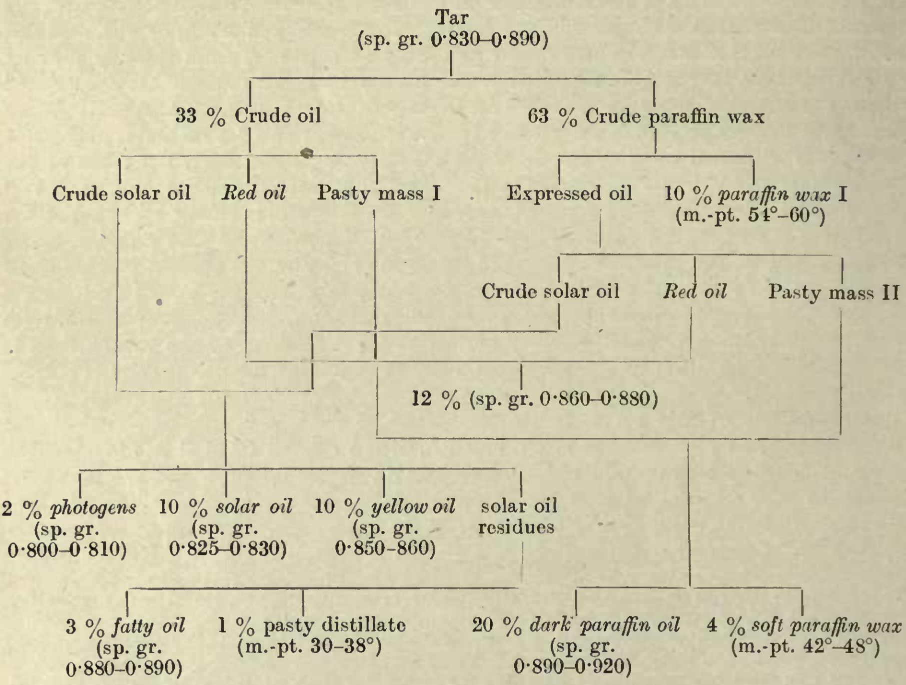
The waste *black acids* may be used for making fertilisers (superphosphates, etc), while the acid resins and pitches may be redistilled to the extent of two-thirds, the remaining one-third serving as tar (goudron) or, if denser, as asphalte. Sometimes, however, these resins and pitches are mixed with alkali creosotes, the water (which contains sodium sulphate) being removed and the resin distilled, while in some cases they are pulverised by means of steam and burnt under the boilers (calorific power, 8000 cals.). The alkali creosote may also be used for impregnating pit-props, or *crude creosote* may be liberated by treatment with dilute sulphuric acid or carbon dioxide (flue gases). Acid pitch may be obtained by diluting the black acid mass with water, since it is not soluble in dilute acid. The pitchy and *resinous masses* which separate may be distilled again, various products (*see later*) being obtained.

Fairly pure concentrated sulphuric acid may be recovered (according to U.S. Pat. 956,276, 1910) from the black acid by allowing it to fall in a thin stream into a retort containing pure sulphuric acid heated to boiling, the acid distilling off being condensed in the usual way (*see* Vol. I., p. 308). This acid may also be decomposed in the hot to obtain SO_2 (U.S. Pat. 956,184, 1910).

in other cases only the benzines (*photogens*) and the light oils are distilled, the residue being cooled to a low temperature and the solid paraffin wax which separates centrifugated to eliminate the tar and heavy oils. When the tars are very dense (above 0·900) Krey finds it convenient to distil them under a pressure of about 10 atmos., thus raising the temperature to 400° to 450°. This yields 60 per cent. of distilled oil of sp. gr. 0·830, which is largely used for the preparation of oil-gas (*see* p. 64), 10 per cent. of gas, and 30 per cent. of residual oily tar.

(2) With light and very pure tars a greater yield of paraffin wax is obtained more cheaply by treating the tar directly with concentrated sulphuric acid, washing with water, and subjecting to fractional distillation over calcium hydroxide. Crystallisation, pressing, and bleaching are carried out as described above.

The following scheme shows the different operations, and the final yields in a tar distillation (the brackets unite products which are worked up together, generally by distillation; the ultimate products are shown in italics):



Photogen is a species of benzine similar to that of petroleum, but obtained by the distillation of wood, lignite, and coal; it is used in the purification of paraffin wax, in the carburetting of lighting gas, and for removing spots from fabrics. *Yellow oil* is used for the extraction of fats and for cleaning; *red oil* (sp. gr. 0·860 to 0·880) has various uses, and serves well for the manufacture of oil-gas (*see* p. 64); the fatty oils and dark paraffin oils (0·880 to 0·925) are used as *oil for gas* [1] and for making *carl-grease;* the yellow and red oils (0·880 to 0·900) are used as thinner lubricants.

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[1] **Oils for Gas.** From the time when gasworks began to mix gas obtained by the carbonisation of bituminous coal with carburetted *water-gas* and with *oil-gas* (in 1905 Germany produced 30,000,000 cu. metres, England 500,000,000 cu. metres, and the United States 1,550,000,000 cu. metres of carburetted water-gas), the use of mineral oils for carburetting the water-gas and for producing oil-gas has increased considerably. These oils for gasifying are obtained partly by the distillation of lignite and shale tars (*see above* and p. 102), but more especially by the distillation of petroleum residues (*solar oil*, intermediate to true petroleum and lubricating oils). The value of these oils increases with the narrowness of the temperature limits within which they boil; these limits are usually 100° apart, and it is of no consequence whether they be 200° and 300°, or 250° and 350°; they should contain less than 25 per cent. of unsaturated hydrocarbons (soluble in concentrated sulphuric acid of sp. gr. 1·83), otherwise they give too much tar and coke on gasification; they should contain not more than 30 per cent. of creosote, but a high proportion of paraffin wax is advantageous. In the United States 600,000 tons were consumed in 1908;

The washing of tar and of its distillates with alkalies and acids yields resinous masses with varying proportions of creosote oil and distillation of these at different temperatures yields *goudron* or *asphalte tar*, or *artificial bitumen*,[1] which is used in the manufacture of *impermeable*

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about 220,000 tons were imported into England in 1906, 320,000 in 1909, and 260,000 in 1910; about 4153 tons of mineral oil (sp. gr. 0·83 to 0·88) were imported into Germany in 1906, 29,600 in 1908, and 46,500 in 1910 for the carburetting of water-gas; Germany itself produces a further quantity of about 300,000 tons of oil for gasifying, 13,000 tons being used for producing oil-gas on the railways, and 9000 tons for mineral-oil engines. For the carburetting of gas these oils should cost less than £4 16*s.* per ton. The amount of *cart-grease* imported into Italy is about 300 tons per annum, and that exported about 120 tons (£800).

[1] **Asphalte, Pitch, and Bitumen.** When *tar from the distillation of wood* (or lignite) is heated until all the volatile products are eliminated, there remains a black mass which, when cold, assumes a glassy consistency and forms *pitch*, used particularly for caulking ships, for preparing shoemakers' thread, and for making cements impermeable to water, etc.

When *coal-tar* is completely distilled it leaves a more or less hard black residue—*coal-pitch*—which is used for ordinary asphalting and for making varnishes, lacs, and coal briquettes (*see* Vol. I., p. 459). Pitch is also prepared expressly by prolonged heating of tar in a current of air or with sulphuric acid.

Bitumen (*mineral pitch*) bears sometimes the unsuitable name, *natural asphalte*, and forms a brittle, blackish brown mass, which, on heating, softens between 100° and 135°; it has the sp. gr. 1·10 to 1·20 and the hardness 2. It burns readily, with a very smoky flame, is insoluble in water, alkali or acid, slightly soluble in alcohol or ether, and readily soluble in benzene, carbon disulphide, and turpentine (in which it ceases to be soluble after exposure to light, and is hence used in photo-lithography). The best bitumen is found at the surface of the Dead Sea in Palestine, and in greater quantities at the *Pitch Lake* in the island of Trinidad, this having an area of 50 to 60 hectares (120 to 150 acres) and a depth of 50 metres, and forming a fairly hard mass; it abounds also in Syria, Utah, Venezuela, and Cuba, and at Dax (France). That of Trinidad contains 40 to 50 per cent. of pure bitumen and 30 per cent. of mineral substances, the remainder consisting of organic substances and water (about 25 per cent.). It is broken up on the spot by means of hatchets into brownish-black lumps permeated with bubbles and is heaped up, the interstices then gradually filling. The rights of working belong to the New Trinidad Lake Company, which pays 5*s.* per ton to the British Government. By means of a telferage line 1 kilometre in length, it is carried to the port, where it is roughly refined by melting at 160° to 170° in open vessels heated with steam coils to separate part of the mineral substances, water and volatile matter, the product thus obtained containing 56 to 58 per cent. of pure bitumen, having the sp. gr. 1·40 to 1·43 and softening at 85° to 95°; the portion soluble in petroleum ether bears the name *petrolene*, and consists of liquid hydrocarbons of the C_nH_{2n-4} series, whilst the insoluble part is known as *asphalte* and is composed of solid substances, which are partly oxygenated and undergo oxidation in the air. Up to the present time this lake, which is partly covered with vegetation, has yielded over a million tons of asphalte and its level has been lowered about 1·25 metres; nowadays about 250,000 tons of bitumen are extracted from it per annum.

The amount of change, or efflorescence, which bitumen will undergo under the action of air and light may be estimated by determining the proportions of *carbenes* present, *i. e.*, the products insoluble in carbon tetrachloride, but soluble in carbon disulphide.

Pure bitumen is used for making black sealing-wax, black lacs, and varnishes, and also lamp-black; the lower qualities serve for coating wooden structures (boats, telegraph poles), for cardboard, for roofs, and damp walls, etc. (*see later*).

In order to distinguish natural from *artificial bitumen*, about 1 gram of the substance is heated to 200°, cooled, powdered, and treated with 5 c.c. of 80 per cent. alcohol; if the latter turns yellow and exhibits fluorescence, artificial bitumen is indicated, whilst if the alcohol remains almost colourless, the bitumen is natural.

By the term *asphalte* (natural) is meant minerals, porous rocks, and earth containing bitumen. *Bituminous rocks* are slightly porous and the bitumen they contain (10 to 15 per cent.) easily flows away when they are heated in suitable furnaces. *Asphaltic rocks*, however, are porous limestone impregnated with bitumen (6 to 12 per cent., or even over 20 per cent.), which does not flow away on heating: they are used for the preparation of *asphalte mastic* by powdering and fusing them homogeneously with a certain quantity of bitumen. This mastic is cooled in moulds and is used directly for paving streets and terraces, either alone or mixed with fine sand or gravel. Powdered asphalte may also be used for paving, by spreading it out hot and compressing it with heavy cast-iron double rollers heated inside.

In California, large quantities of *artificial asphalte* are prepared by prolonged injection of air into dark mineral oils (sp. gr. 0·9333 to 0·9859) heated at 650°. Fusion of colophony at 250° and addition of sulphur yields an asphalte which is similar to that of Syria and is used in photography.

Natural asphalte occurs abundantly near Neuchâtel, in the Department of Ain (France), in the neighbourhood of Hanover, and in Italy at Lettomonapello (the product of this locality is worked at S. Valentino, near Chieti), and especially at Ragusa and Castelluccio, near Modica (in the Sicilian province of Syracuse). These Sicilian asphalte rocks consist of pure, more or less hard chalk, impregnated with 7 to 14 per cent. of bitumen, and until 1858 were used solely, and to-day are used partly, for the manufacture of building stone. Almost the whole of this rock is exported, the exportation amounting to 1782 tons in 1878, 2186 in 1882, 26,587 (£26,587) in 1894, 12,140 in 1897, 47,440 in 1899, 55,307 in 1903, 72,746 in 1905, 89,808 (£88,012) in 1908, *pasteboard* for roofing, in rendering woodwork and masonry (especially in damp houses) damp-proof, and also in the manufacture of ultramarine.

III. Another important source of *paraffin wax* is furnished by the **Bituminous Schists**, which are especially abundant in the Lothians in Scotland (at Broxburn, Bathgate, etc.), where at depths of 600 to 1200 metres layers 2 to 4 metres in thickness are found over an area 95 kilometres long and 8 to 13 kilometres wide.

In 1848 Young and Meldrum began to work and purify a special oil issuing from the surface of the soil in Derbyshire (*see* note, p. 66), and, having exhausted this deposit and not finding others, they succeeded in preparing mineral oils, which had been already introduced for illuminating purposes, by distilling cannel coal, which gave much lower but remunerative yields.

In about 1860 they discovered that the interesting Scotch deposits of boghead coal gave a yield of oil much greater than cannel coal, and in 1864 and 1866 were erected the two works at Bathgate and Addiwell, which became world famous. The deposits of boghead coal were exhausted in four or five years, and were then replaced by the more abundant, although less fertile, deposits of *bituminous schists* (*shales*) in which Scotland is so rich. These shales have been formed by the slow deposition of fish at the bottom of

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and 85,947 (47,759 to Hamburg, 10,125 to London, 4040 to Buenos Aires, 3800 to Antwerp, 3000 to New York, 2800 to Rouen, 2720 to New Orleans, 2605 to Rotterdam, 2537 to Greece, 2014 to Alexandria, 1707 to Hungary, 1050 to Calcutta, etc.) in 1909. The mean *price* of the rock at the port is £1 per ton. These Sicilian deposits were studied by Della Fonte and Moschini in 1884, Ragusa in 1901, Manzella in 1906, Maderna in 1906 and 1909, and Coppadoro and Schiavo-Leni in 1908–1910. For *street paving* these powdered rocks should contain less than 2 per cent. of residue insoluble in hydrochloric acid (clay and silica) and should be free from pyrites (in the air this is converted into soluble ferrous sulphate, which results in disintegration of the pavement); the proportion of bitumen (extracted by chloroform from the well-powdered material, dried at 100°, in a Soxhlet apparatus) should be more than 8 per cent. and less than 13 per cent. Various firms export asphalte ready powdered from Sicily and manufacture *asphalte mastic* (*see above*) by mixing, in the hot, powdered asphaltic rock with either Trinidad bitumen or bitumen obtained by distilling the richer rocks (12 to 25 per cent. of bitumen).

By the name *asphaltite* are known certain bitumens found naturally in veins and among these Marcusson (1914) includes Syrian asphalte or bitumen, Gilsonite, Grahamite, and Albertite. These are more expensive than other bitumens, and, being harder and more shiny and more easily powdered, are used more especially in the lac industry. They are distinguished chemically from asphaltes and bitumens by their content of organic acids, organic sulphur and matter soluble in CS_2 and CCl_4. As they contain less than 7 per cent. of oils resistant to sulphuric acid, they are to be regarded as products of more advanced decomposition than bitumen.

STATISTICS AND PRICES. The Italian output of asphaltes and bitumens is as follows (tons):

	1910	1912	1913	1914	1915	1916	1917
Natural asphalte rock . .	162,212	181,397	171,097	119,853	47,650	16,829	—
Powdered asphalte rock .	26,137	34,648	40,573	17,200	11,279	5,607	—
Asphalte in cakes (bituminous mastic)	13,953	16,612	13,961	13,772	11,460	8,477	—
Artificial asphalte . .	8,580	6,200	6,000	4,700	—	—	—
Compressed asphalte bricks .	943	1,164	1,790	2,249	2,187	1,618	—
Crude bitumen . . .	457	549	393	326	355	786	—
Refined bitumen . .	672	283	426	531	775	960	—
Solid bitumen, importation .	3,365	3,548	4,300	2,924	4,139	1,090	1,381
,, ,, exportation .	26,125	13,158	6,596	6,367	6,720	121	111

The production of *pitch* in Italy was 7220 tons in 1909, 11,964 (£25,920) in 1912, 17,746 in 1915, and 30,182 (£122,668) in 1916.

Great Britain imported 68,389 tons of asphalte and bitumen in 1909 and 69,398 tons (£168,000), together with 12,000 tons of pitch (excluding that from coal tar), valued at £66,000 (the exports being of the value £720,000), in 1910. The output of oily shales was 2,967,700 tons in 1909, 3,130,000 (£430,000) in 1910, 3,280,143 in 1913, and 3,268,666 (£837,240) in 1914.

In Germany there were fifteen works treating asphalte rocks (costing about 8*s*. 6*d*. per ton) in 1910, the quantity treated being 76,964 tons (giving 4400 tons of asphalte) in 1909, and 81,335 tons (giving 4640 tons of asphalte) in 1910. The imports were 130,062 tons in 1908 and 98,370 (exports 14,200 tons) in 1909; 103,000 tons were produced in 1905, 89,000 (£40,000) in 1908, and 77,500 in 1909.

The *prices are:* for the tar (goudron), £3 5*s*. per ton; Archangel pitch, I, £11 4*s*.; Swedish pitch, £9 4*s*.; coal pitch, £2 to £2 8*s*.; lignite pitch, £2 8*s*. to £3 4*s*.; stearine pitch, £7 4*s*. to £14 8*s*.; Syrian asphalte, I, £34; asphalte in fine powder, £70.

the sea, with interposition of deposits of clay, which even now bears the imprints of the fish. They are greyish-black or brownish, with a lamellar structure, and have the sp. gr. 1·71 to 1·87.[1]

The invasion of American petroleum in about 1880 created a serious crisis in this industry, which was partially saved by new and improved technical methods introduced by engineers and chemists, especially by Beilby, Henderson, Crichton, and Bryson; the by-products were more completely utilised, the furnaces improved, fractional distillation apparatus brought into use, the ammoniacal liquors utilised, the tar, coke, gas, and final residues employed as fuel, and the labour reduced to a minimum; the mineral oil came to occupy a secondary position, attention being paid to the production of paraffin wax and high-class lubricating oils for engines.

The furnaces and retorts used in Scotland for the distillation of bituminous shale have undergone continuous improvement. Horizontal retorts gave way to vertical ones, and of these the most perfect types are the Henderson retorts, brought into use in about 1895 at Broxburn, and the Bryson retorts, applied later at Pumpherston, both being modifications of the old vertical retorts of Young and Beilby (called also Pentland retorts). The furnace with Bryson retorts is shown in Fig. 103. The retorts are 9 metres high, have a circular section with a mean diameter of 90 cm., and hold 4·5 cu. metres of shale in lumps of walnut size (the old Henderson retorts contained 3 and the old Pentland retorts 1 cu. metre). The lower

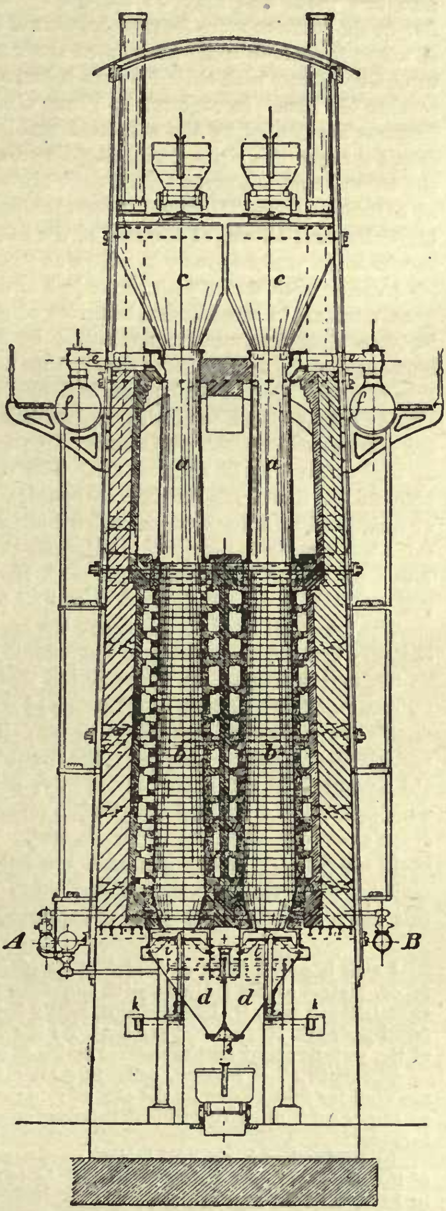

FIG. 103.

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[1] In France these bituminous schists, which abound in the basin of the Autun and at Buxière-les-Mines, form two strata which are 1 to 2 metres thick and extend over an area of 18,000 hectares (44,460 acres), the best deposits being at a depth of 80 metres. They were first worked in 1837 by Selligne in consequence of the studies of Reichenbach (1830), and the industry became a flourishing one about 1860; in 1864, 128,550 tons of shale were distilled, producing 4750 tons of crude oil, destined principally to prepare oil-gas in the large towns. The invasion of American petroleums also overthrew this industry, which now survives on account partly of the Customs duty and partly of the adoption of Scotch distillation furnaces (Fig. 103), which give improved yields.

In Australia, especially in the neighbourhood of Sydney, extensive deposits (from a few centimetres to 2 metres thick) of bituminous shale occur which, according to Potonié, originated in oily algæ, and are hence to be regarded as coals rather than as shale. On distillation they give 68 per cent. of oils, 14 per cent. of gas, 11 per cent. of crude paraffin wax, and 7 per cent. of ash.

A bituminous schist from Midlothian (Scotland) gave on analysis: 20 per cent. carbon, 0·7 per cent. nitrogen, 1·5 per cent. sulphur, the rest being mineral matter; it gave up nothing soluble to ether. Another sample showed 2·7 per cent. water, 24·3 per cent. tar, and 73 per cent. residue (ash). Certain French shales give only 5 to 6 per cent. of tar, whilst those from Australia give as much as 60 per cent., but are poor in paraffin wax. Unlike that of bituminous lignites, the tar of shale cannot be extracted by solvents.

two-thirds, *b*, of the retorts is of refractory bricks (chamotte) and the upper part, *a*, of cast-iron fixed with mastic into the chamotte part. The shape is slightly conical, and at the upper end is a large sheet-iron hopper, *c*, containing sufficient broken shale to feed the retort for twenty-four hours. The mouth at the bottom of the retort is restricted somewhat and is closed with a hinged grid or disc, which is divided into two parts and may be opened by the lever arms, *k*, so as to discharge, every five to six hours or more frequently, part of the exhausted shale into the sheet-iron hopper, *d*, where it cools to some extent; at the same time fresh material enters the retort at the top. The retorts with their hoppers below are united in pairs, a single discharge orifice, *s*, serving the two. In each retort 5 tons of shale are distilled per twenty-four hours. The furnaces are heated by the non-condensable gases from the distillation, these being introduced through the pipes *A* and *B*. The distilled products are evolved at the top through the tubes *e* and are aspirated through the tubes *f* to the condensing plant. This consists of batteries of vertical wrought- or cast-iron tubes, which are 60 cm. in diameter at the beginning and 45 cm. at the end of the battery and rest on adjacent but separate tanks, in which the various products collect as they are gradually condensed by the cold external air (cooling with water with the object of diminishing the number of tubes has not given good results; in some cases, batteries of small air-cooled tubes are used). Batteries of forty to sixty furnaces are controlled by four workmen by day and two by night (the hoppers, *c*, are charged during the daytime). The gases heating the retorts have a temperature of about 700° at the bottom and 400° at the top, flow of the bitumen before distillation and the production of obstructions being thus avoided. In some instances the retorts are also heated internally by means of superheated steam. With regular working 100 kilos of shale give 8 to 10 kilos of tar. The yield is about 6 per cent. of gas, 8 per cent. of ammoniacal liquor (ammonium carbonate), 12 per cent. of crude oil (tar), and 7 per cent. of residue (4 to 5 per cent. of which consists of combustible matter). The crude oil contains less than 0·03 per cent. of sulphur; the gas evolved contains 21 to 23 per cent. CO_2, 1 to 4 per cent. CO, 12 to 24 per cent. H, 1·6 per cent. of heavy hydrocarbons, 8 to 20 per cent. CH_4, 1·2 to 4 per cent. O and 35 to 43 per cent. N.[1]

The crude oil is dark green, has the sp. gr. 0·865 to 0·895 at 44°, and is semi-solid at ordinary temperatures owing to the paraffin wax present.

This oil is treated by virtually the same methods as are used for lignite tar, that is, by continuous distillation in a current of steam, so as to obtain purer products. The first distillation gives: *green naphtha* (0·753) and *green oil* (0·858), which are purified by acid and alkali and then redistilled: the first gives commercial mineral oil (also solar oil) and the second light oils and paraffin wax, which is separated by cooling from the *blue oil*, which serves as a good lubricant when refined. The paraffin wax is purified by the process given above (paraffin wax of lignite tar). The gas evolved during the distillation of crude shale oil showed, in one instance, the following percentage composition: heavy hydrocarbons, 14·5; methane, 59; ethane, 26·5; hydrogen, traces; CO, CO_2, and O, nil. When this gas is cooled, a light benzine for automobiles is obtained.

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[1] One hundred kilos of Scotch shale gives on distillation in modern furnaces as much as 30 cu. metres of *gas* (only 14 with the older furnaces) containing, for instance, 22·08 per cent. CO_2, 1·18 per cent. O, 1·38 per cent. heavy hydrocarbons, 9·77 per cent. CO, 3·70 per cent. CH_4, 55·56 per cent. H, and 6·33 per cent. N; the very high content of hydrogen is due to the action of the water-vapour on the red-hot residues of the shale.

The distillation *residues*, consisting almost entirely of mineral matters, have no value, and are used for filling holes in the ground; in some few cases, the residues (coke) contain as much as 12 per cent. of combustible substances and are then mixed with better fuel and burnt in the furnaces.

In 1876, when horizontal retorts were used, the *cost* of 100 litres of tar, including the value of the raw shale, was estimated at 8*s.*; in 1879, with Henderson vertical retorts, at 4*s.* 6*d.*, and in 1897, with the new retorts, at 3*s.* 6*d.*

The gases used for heating the furnaces consist of 80 per cent. of water-gas and 20 per cent. of distillation-gas and tar vapours (2 per cent.). In some modern works the quantity of gas is increased by passing steam in at the bottom of the furnace, this, with the carbon remaining in the hot, exhausted shale, giving water-gas rich in hydrogen and carbon monoxide.

The *waters* distilled from shale form three-fourths by weight of the distillate have the sp. gr. 4° Bé., and contain ammonia and pyridine. The ammonia is recovered as crystallised sulphate by the method used in gasworks. Each ton of shale gives 5 to 6 kilos of ammonium sulphate, which in many factories is the sole source of profit. Benzene is also obtained from the gas by washing the latter with paraffin oil in a coke tower or scrubber.

A ton of bituminous schist (of the value of 12*s.* 9*d.*) yields about 8 kilos of naphtha, 115 kilos of crude oil (green oil), and 13 kilos of ammonium sulphate. From 100 kilos of green oil are then obtained 31 kilos of burning oil, 13 kilos of lighting oil, 11 kilos of middle oil, 15 kilos of paraffin wax, and 15 to 20 per cent. of gas, water, and loss, the remainder being coke (about 3 per cent.), which is used as a black pigment.

In 1873, 524 tons of oily shales were treated in Scotland, in 1893 about 2,000,000 tons, and in 1909 3,000,000 tons, giving 280,000 tons of crude oil. The Scotch shale-oil refineries produced in 1908 90,000 tons of burning oil, 16,000 tons of engine oil, 40,000 tons of gas-oil, 40,000 tons of lubricating oil, 25,000 tons of paraffin wax, and 60,000 tons of ammonium sulphate. In 1908 134,163 tons of bituminous shale, of the value £72,400, were produced in Italy. In France 219,000 cubic metres were distilled in 1890.

In Germany 80,000 tons of lignite tar (corresponding with 600,000 tons of lignite) are distilled annually, and the products obtained (9000 tons of paraffin wax—two-thirds hard and one-third soft—5000 tons of solar oil, and 3500 tons of heavy oil) have a value of about £880,000.[1]

Tar can be purchased from the lignite distilleries at little more than 10*d.* per quintal (2 cwt.) and, treated as above, yields 14*s.* 5*d.* to 16*s.*, taking as the average selling prices per quintal: paraffin wax, £3 12*s.*; solar oil, 10*s.* 5*d.*; yellow oil of paraffin, 12*s.* 10*d.*; dark oil of paraffin, 10*s.* 5*d.*

The competition of the Galician product lowered the price of paraffin wax in 1910 and 1912 to £20 per ton. In various countries there are special bituminous shales which have originated from the decomposition of immense heaps of fish accumulating at the bottom of former seas, the decomposition products being interlayered with clay and then carried by geological convulsions to the surface of the earth and to the summits of mountains. These shales abound in the residues of numerous different fish and also in vegetable débris, and the bitumen or oil obtained from them by distillation contains large proportions of organic sulphur (2 to 10 per cent.) and nitrogen (24 per cent.), which impart to the crude oil an unpleasant odour and a deep brownish-yellow colour with greenish reflection.

The most important deposit of these ichthyolic shales, which are worked industrially for the preparation of ichthyol[2] (used extensively in medicine, especially for the treatment

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[1] The *bituminous coal of Messel* (*see* note, p. 94) is utilised in a special way, the vapour derived from the drying of the coal being employed in the upper part of the vertical retort to produce water-gas. The vapour is injected by means of a blower into the bottom of the retort, where it meets red-hot coke, all the nitrogen of the latter being transformed into ammonia, which issues with the water-gas and the vapours from the distillation at a point about one-third up the retort (Ger. Pat. 200,602, 1906). This process for utilising the nitrogen of the coke is derived from that patented by A. Grouven in 1878 (hence prior to the Mond process) for the utilisation of the nitrogen of peat. To fix the ammonia of the gases and vapours, these are passed into a species of Glover tower, in which they are washed by a spray of dilute sulphuric acid, the ammonium sulphate solution obtained being concentrated to crystallisation by means of the heat of the furnace and of the distillation products, which are thus appreciably cooled. The tar from the Messel coal has the sp. gr. 0·855 to 0·860 at 44°.

[2] Ichthyol is an oil of sp. gr. 0·865 which is obtained between 100° and 255° during the dry distillation of ichthyolic bituminous shale. On distillation it yields, besides a highly luminous gas, 5 to 7 per cent. of crude ichthyol. On distillation, these shales lose 30 to 40 per cent. of their weight. The Besano oil is richer in pyridine bases than that of Seefeld, which contains 1 per cent. of them (Baumann and Schotten, Contardi and Malerba).

Treatment of this oil (when redistilled it is almost colourless and contains 2·5 per cent. or more of sulphur) with concentrated sulphuric acid yields *ichthyolsulphonic acid* containing 10 to 15 per cent. S (like sulphoricinates) and forming salts (*ichthyolsulphonates*) with soda, or better with ammonia, which are used in the cure of skin diseases. *Ammonium ichthyolsulphonate* ($C_{22}H_{36}O_6S_3(NH_4)_2$?), which commonly bears the name of *ichthyol*, forms a dense, reddish brown liquid, soluble in water, and its solution gives a black resinous deposit with HCl and yields NH_3 when treated with KOH; it dissolves also in a mixture of alcohol and ether.

When heated in the air it burns without leaving a residue, while at 100° it does not lose more than 50 per cent. of its weight (water). If a current of steam is passed on to the surface of boiling ichthyol, the latter is rendered almost odourless (Knoll & Co., Ger. Pat. 118,542, 1899), but deodorisation with hydrogen peroxide destroys the medicinal properties; the deodorised product is termed *desichthyol.*

The best qualities of ichthyol contain between 3 to 5 per cent. and 8 per cent. of sulphur as sulphonic group and between 4·5 per cent. and 14 per cent. of sulphur as SH, the total sulphur amounting to 12 to 18 per cent. and the combined ammonia to 2·5 to 4·3 per cent. *Anitine* is an ammonium ichthyolsulphonate purified by means of alcohol; its aqueous solution dissolves of painful sores and inflammations) occur at Seefeld and at Reith, near Innsbruck in the Tyrol; similar deposits are found in various parts of Italy.

IV. Another source, one of the most important, of *paraffin wax* is Ozokerite (or *mineral wax*). It is found in England, Russia, and America, but the deposits of greatest industrial and historical importance are those of Galicia (that of Boryslaw gives 3000 tons and that of Dzwiniacz about 1000 tons per annum, while those of Pomiarki and Starunia are of inferior quality), where it occurs in seams as much as a metre in thickness. It was discovered by Doms when searching for petroleum, and from 1860–1870 was worked by the Landesberg process for the extraction of a kind of paraffin wax, which competed keenly with that of Saxony and Thuringia (from lignite, *see* p. 95); in 1870, Pilz and Ujhelyi found that simple treatment of ozokerite twice with concentrated sulphuric acid, followed by decolorisation with prussiate black (*see* Vol. I., p. 840), yields *cerasin*, a product of greater value than, and similar to, beeswax.[1] In the State of Utah, the industrial treatment of ozokerite was begun in 1888, and in 1890 already yielded as much as 600 tons of crude cerasin.

In recent years the decolorisation of ozokerite has been simplified, but whereas with paraffin wax fuller's earth (*see* Vol. I., p. 738; also this Vol., chapter on Vegetable Oils) may be used as a decolorising agent in place of prussiate black (which is increasing in price owing to diminished production), this does not serve in the case of cerasin. A special decolorising material, termed *francolite* or *tonsile*, gives, however, complete decolorisation at one-half the cost, after a single treatment of the ozokerite with sulphuric acid; extraction of the decolorised residues with benzine is then somewhat difficult, but the difficulty is overcome by using trichloroethylene (*see* p. 122), which is denser, and by extracting in lead-lined apparatus.

Ozokerite forms an amorphous mass of a yellow, brown, greenish, or black colour and of varying consistency; the harder varieties show a fibrous fracture; the specific gravity is 0·85 to 0·95, and the m.-pts. of the various commercial varieties are 84° to 86°, 65° to 76°, and 55° to 65°; these contain less than 5 per cent. of moisture and volatile products. Pure ozokerite contains 85 to 86 per

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many substances insoluble in water (camphor, volatile oils, phenol, etc.). The ichthyolsulphonates of the heavy metals are only slightly soluble in water.

Of the many other derivatives (and substitutes, *e. g.*, *thyol*, obtained by treating tar-oils with sulphur), mention may be made of *ichthyoform* (blackish brown, inodorous), prepared by treating ichthyolsulphonic acid with formaldehyde and used as an antiseptic for the intestines and instead of iodoform for curing wounds; it costs £4 per kilo and ammonium ichthyolsulphonate £1 per kilo.

[1] The material from the mines (shafts 80 metres or more in depth), which contains admixed earth and stones, is placed in open vessels holding 300 litres and heated by direct fire heat; the mineral matter settles to the bottom and is separated by decantation. This matter still contains 10 per cent. of wax, which is extracted with benzine (*extraction wax*); both this and the decanted part (*fusion wax*) form the prime materials treated in the refineries found in all countries.

The refining is carried out in large iron boilers holding up to 3000 kilos of the crude wax, half a metre being left free to take the scum which forms. The fused mass is kept at 115° to 120° for four to five hours and is stirred to liberate all the water; 15 to 25 per cent. (according to the quality of the wax) of fuming sulphuric acid containing 65 per cent. of free SO_3 is then added, in a thin stream, to the mass, which is thoroughly stirred meanwhile; the temperature rises slowly to 165° and then to 175°, with vigorous evolution of SO_2 and formation of froth, which may overflow and take fire if the hearth is not well isolated. The oxidisable impurities separate as a black mass (*asphalte*) and the excess of sulphuric acid evaporates. The vessel is covered and provided with a draught-pipe to carry off the acid vapours. When emission of SO_2 ceases, the mass is heated to 180° to 200° and then allowed to cool slowly, being neutralised and decolorised with 5 to 6 per cent. of *cyanide black* [which is the residue from the old method of making yellow prussiate (*see* Vol. I., p. 840) and contains animal black, alkaline earth carbonates and phosphates, and iron oxide and sulphide] or with blood carbon, and is sent hot to the filter-presses. The mass obtained is still slightly yellow and is whitened by further treatment with sulphuric acid. When beeswax is to be imitated, turmeric, quinoline yellow or other coal-tar dye is added, together with a little Peru balsam to impart the required odour. The filter-press residues are mixed with sawdust or, better, with rice husks, and extracted with benzine to recover all the cerasin; after recovery of the benzine, the insoluble residue is used as fuel.

cent. of carbon and 14 to 15 per cent. of hydrogen, and hence consists principally of paraffins, together with a small proportion of olefines; it is soluble in benzine, turpentine, petroleum, ether, and carbon disulphide, but only slightly so in alcohol. It forms an excellent electrical insulator, and may be used in place of gutta-percha.

According to Höfer, ozokerite has been formed by the slow evaporation, during many centuries, of petroleum rich in paraffin wax.

On distillation it yields: 2 to 8 per cent. of benzine, 15 to 20 per cent. of naphtha, 36 to 50 per cent. of paraffin wax, 15 to 20 per cent. of heavy oils, and 10 to 20 per cent. of residual solids.

STATISTICS AND PRICE OF PARAFFIN WAX. The importation of paraffin wax, cerasin and vaseline into Italy was as follows (tons):

	1905	1908	1910	1912	1913	1914	1915	1916	1917
Paraffin wax .	8878	11932	19153	25584	24557	21042	32436	33638	26278
Cerasin . .	41·7	111	88	110	76	89·3	40	18·5	3·2
Vaseline .	—	110·5	109·4	124	109·4	84	116	288	471

In 1908 fourteen factories in Germany treated 70,000 tons of lignite tar, worth about £160,000, and produced 45,000 tons of oil, 11,000 tons of crude paraffin wax (equal to 7600 tons of the pure wax, worth £220,000), and 8000 tons of creosote, tar, and pitch, of the total value of £450,000; about 1,000,000 tons of lignite were distilled and 350,000 tons of coke left. For several years, however, the industry has been stationary. In 1910 Germany imported 17,000 tons of paraffin wax and wax candles, besides 46,500 tons of gas-oil. In order to offer more effective resistance to the crushing competition of Austria (Galicia), the five largest German works combined in 1913, with a capital of more than £3,200,000, three small factories remaining outside of the combine.

France imported 624 tons of ozokerite in 1913, 483 in 1914, and 335 in 1915.

Galicia produced 2116 tons of ozokerite and 62,000 of paraffin wax in 1910.

The United States exported 75,000 tons of paraffin wax in 1905, 90,000 in 1910, and 96,000 (£1,440,000) in 1911; 95 per cent. of the American output is in the hands of the Standard Oil Company.

The petroleum of Tscheleken (Russia) contains up to 8 per cent. of paraffin wax and is treated in a Baku works, which produced 34 tons of wax in 1908, 160 in 1909, 600 in 1910, and 700 in 1911.

In 1907 Great Britain produced 3500 tons of paraffin wax, and in 1909 imported 50,000 tons (£1,400,000) and exported 17,000 tons (£408,000); in 1910, 14,000 tons were exported. The Scotch shales yielded 23,000 tons of paraffin wax in 1910.

Spain imported paraffin wax to the value of £90,400 in 1909 and £112,000 in 1910.

The market *price* of paraffin wax varies somewhat with its melting-point: first quality white, m.-pt. 38° to 40°, costs £39 per ton; that with m.-pt. 42° to 44°, £41; m.-pt. 48° to 50°, £43; m.-pt. 56° to 58°, £46; m.-pt. 60° to 62°, £50. That used in pharmacy, m.-pt. 74° to 76°, costs as much as £96, and the crude wax about £29. For some years before the war the price was lowered considerably, owing to the large output in Galicia, whence it was exported even at £16 per ton.

Pure white *cerasin* resembles wax, melts at 62° to 80°, has the sp. gr. 0·918 to 0·922, and is dextro-rotatory. It is used in making candles, in perfumery, as dressing for textiles, in making boot- and floor-polish, waxed paper, pomades and cosmetics, crayons, etc. It is subject to much adulteration [1] owing to its high price. Before the war, first quality yellow cerasin, m.-pt. 62° to 63°, cost £54 per ton; second quality, £46; that with m.-pt. 68° to 70°, £60, and the white variety, m.-pt. 52° to 63°, £66.[2]

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[1] The *analysis* of paraffin wax, vaseline, cerasin, mineral oils, etc., is described in treatises dealing with the analysis of industrial products, *e. g.*, Villavecchia's "Applied Analytical Chemistry," Vol. I.

[2] A *mixture of cerasin and paraffin wax* may be detected by the following tests: a glass rod 3 mm. in diameter is immersed to a depth of 1 cm. in the fused substance, extracted, allowed to cool, and hung in a test-tube heated externally with water. If the wax drops above 66°, it is pure cerasin, whereas if it drops below 66° it is regarded as mixed with paraffin wax or as the latter alone. The dropping-point may be determined also with the Ubbelohde apparatus (p. 6). Addition of colophony is recognised by the *acid number* or saponification number, colophony being saponifiable and cerasin not.

Cerasin has been made in continually diminishing quantity since 1913, owing to its cost, and even in making candles has been replaced more or less completely by paraffin wax. The high price of cerasin depends on that of ozokerite, which is now partially exhausted and occurs to some extent at great depths (300 metres at Boryslaw and 100 metres at Dzwiniacz).

The *ozokerite* worked in Austria-Hungary in 1877 amounted to 8961 tons; in 1885, 13,000 tons; and in 1894, 6742 tons. The exportation of cerasin was 3594 tons in 1891, and 2382 tons in 1895.

In the United States the production of refined ozokerite, which was 160 tons in 1888, rose in 1892 to 75,000 tons, of the value of £4,000,000.

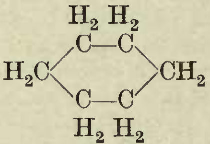
(b) UNSATURATED HYDROCARBONS

I. ETHYLENE SERIES : C_nH_{2n} (Alkylenes or Olefines)

Two groups belong to this series: the *olefine* group, the first member of which is ethylene, C_2H_4, the succeeding ones being open-chain hydrocarbons with a double linking between two carbon atoms, since hydrogen, halogens, ozone, etc., can be readily added to them, transforming them into saturated compounds of the paraffin series.

The other group yields additive products only with difficulty, and its members are formed of closed carbon-chains (*cyclic compounds*). The first term is *trimethylene* or *cyclopropane*, *hexamethylene* and higher compounds being known:

Trimethylene



Hexamethylene

The carbon atoms in these last compounds are all in the same conditions and cannot be differentiated. The cyclic compounds will be studied as a separate section of the aromatic series (Part III).

The following Table gives the more important members of the olefine series (the numbers in parentheses representing boiling-points under reduced pressure):

	Melting-point	Boiling-point		Melting-point	Boiling-point
Ethylene, C_2H_4 .	− 169°	− 103°	Decylene, $C_{10}H_{20}$.	—	172°
Propylene, C_3H_6 .	—	− 48°	Endecylene, $C_{11}H_{22}$.	—	195°
Butylene (3 isoms.), C_4H_8 α	—	− 5°	Dodecylene, $C_{12}H_{24}$.	− 31°	(96°)
β	—	+ 1°	Tridecylene, $C_{13}H_{26}$.	—	233°
γ	—	− 6°	Tetradecylene, $C_{14}H_{28}$.	− 12°	(127°)
Amylene (5 isoms.), C_5H_{10};			Pentadecylene, $C_{15}H_{30}$	—	247°
Normal amylene .	—	+ 35°	Hexadecylene (Cetene) $C_{16}H_{32}$	4°	274° (155°)
Hexylene, C_6H_{12} .	—	68°	Octadecylene, $C_{18}H_{36}$.	+ 18°	(179°)
Heptylene, C_7H_{14} .	—	98°	Eicosylene, $C_{20}H_{40}$.	—	—
Octylene, C_8H_{16} .	—	124°	Cerolene, $C_{27}H_{54}$.	+ 58°	—
Nonylene, C_9H_{18} .	—	153°	Melene, $C_{30}H_{60}$ . .	+ 62°	—

The *official nomenclature* of the olefines is the same as that of the paraffins, excepting that the final *ane* is changed into *ene* (thus ethylene, which is isologous with ethane, is called *ethene*, and so on; *see also* p. 29).

These unsaturated hydrocarbons differ little in their *physical properties* from the corresponding saturated homologues.

The first terms—up to C_4H_8—are gases, and after C_5H_{10} come liquids with increasing boiling-points, these gradually approaching one another as with the paraffins; the higher members are solid and, like the paraffins, have the sp. gr. 0·63 to 0·79, are insoluble in water, but soluble in alcohol or ether.

The chemical properties differ somewhat from those of the saturated compounds. Thus, they readily take up HCl, HBr, HI, Cl, Br, I, fuming H_2SO_4, hypochlorous acid (giving chloro-alcohols or *chlorhydrins*, *e. g.*, $CH_2 : CH_2 + HClO = CH_2Cl \cdot CH_2OH$), hyponitrous acid, ozone, etc., forming compounds of the saturated series.

Cl is added more easily than I (*see* Iodine number: chapter on Fats), Br occupying an intermediate position, whilst HI is added more easily than HBr, and this more easily than HCl. With these acids, the halogen is added to the carbon atom with which the least hydrogen is combined.

Ethylene unites with fuming sulphuric acid at the ordinary temperature and with the ordinary acid at 165°, forming ethylsulphuric acid, $C_2H_5O \cdot SO_3H$; with higher compounds, the acid radicle passes to the less hydrogenated carbon atom.

They often *polymerise* under the action of sulphuric acid or zinc chloride; for example, amylene, C_5H_{10}, forms $C_{10}H_{20}$, and $C_{15}H_{30}$ gives $C_{20}H_{40}$.

They are readily *oxidisable*, for example, with potassium permanganate or chromic acid (not with nitric acid in the cold), the chain being then broken at the double linking, with formation of oxygenated compounds (acids) containing fewer carbon atoms in the molecule. Careful use of permanganate results initially in the addition of two hydroxyl groups without breaking the chain and forming dihydric alcohols (*glycols*), for example, $OH \cdot \underset{|}{CH}—\underset{|}{CH} \cdot OH$.[1]

Almost all compounds with a double linking between atoms of carbon give *Baeyer's reaction*, that is, they rapidly discharge the violet colour of a dilute solution of potassium permanganate and sodium carbonate, with formation of a reddish-brown flocculent precipitate of hydrated manganese peroxide.

This reaction is not given by reducing substances like aldehydes or by certain aromatic compounds (*phenanthrene*, etc.).

With tetranitromethane they give a yellow or brown coloration (the nitro-derivatives and organic acids being exceptions), tautomeric enolic compounds also reacting in this way (*see* p. 18: I. Ostromislenski).

All compounds with doubly linked carbon atoms give the *ozone reaction* (Harries, 1905, and Molinari, 1907), that is, when dissolved in a suitable solvent they fix, *quantitatively* and in the cold, the ozone contained in a current of ozonised air passed through the solution; in this property they differ from compounds with either a triple linking or a benzene double linking (E. Molinari, *Ann. Soc. Chim. Milan*, 1907, 116).

Of interest also are the formolite and nitric acid reactions (*see* pp. 71, 91).

METHODS OF PREPARATION. (1) They are formed, together with petroleum, in the dry distillation of wood, lignite, coal, paraffin wax ("cracking," *see* pp. 87, etc.).

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[1] From what has been said up to the present, it is obvious that a *double linking* does not signify a firmer union between carbon atoms; it is simply a conventional sign. The breaking of the chain, by oxidising agents, at the double linking is to be attributed to the ease of formation of intermediate products (*e. g.*, dihydric alcohols) rather than to a less attraction existing between carbon and carbon at that point. Such readiness to react may, according to Baeyer, be explained by regarding the affinities of the carbon atom as orientated or grouped at four poles arranged like the vertices of a regular tetrahedron (*see* pp. 19 *et seq.*). If two carbon atoms unite by a double linking, the poles at the surface of the carbon atoms become displaced and approach one another, so that there results a certain *tension* which explains the readiness with which the double linking reacts or opens. After the initial oxidation leading to these intermediate products, further action of the oxidising agent, as a general rule, *oxidises or breaks the chain at a point where oxygen already exists, that is, where the oxidation is already begun* (*see* Part III, The Hypothesis of the Partial Valencies of the Benzene Nucleus).

(2) By eliminating water from the alcohols, $C_nH_{2n-1}OH$, by heating them with dehydrating agents (H_2SO_4, P_2O_5, $ZnCl_2$, etc.); a stable intermediate product is sometimes formed, *e. g.*, ethylsulphuric acid, $C_2H_5 \cdot HSO_4$, which at a higher temperature gives ethylene and sulphuric acid. Higher alcohols and ethers are resolved, merely on heating, into olefines and water.

(3) From saturated halogen derivatives, $C_nH_{n+1}X$ ($X =$ halogen), especially from secondary and tertiary bromo- and iodo-derivatives, by heating them with alcoholic potash, or by passing their vapours over heated lime or lead oxide, etc.

$$C_5H_{11}I + C_2H_5OK = KI + C_2H_5 \cdot OH + C_5H_{10}.$$

The mixed ether, $C_5H_{11} \cdot O \cdot C_2H_5$, may also be formed to some extent.

(4) From dihalogenated compounds by heating with zinc:

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(5) By electrolysis of dibasic acids of the succinic acid series:

$$C_2H_4(COOH)_2 = C_2H_4 + 2CO_2 + H_2.$$

(6) Unsaturated compounds are obtained by heating the condensation products of the *ketenes* (*q.v.*).

CONSTITUTION OF THE OLEFINES. In this group it is assumed that between two carbon atoms there exists a double linking: $H_2C = CH_2$, $H_2C = CH—CH_3$, etc., the presence of two free valencies, thus, $\underset{|}{H_2C}—\underset{|}{CH_2}$ or $\underset{\wedge}{HC}—CH_3$, being excluded for the following reasons

In unsaturated compounds the addition of halogen does not take place at a single carbon atom, so that ethylene chloride, $C_2H_4Cl_2$, has not the formula $CH_3 \cdot CHCl_2$, which is that of ethylidene chloride obtained from acetaldehyde, $CH_3 \cdot CHO$, by replacement of the O by Cl_2 (by the action of PCl_5). Since ethylene chloride is chemically and physically different from ethylidene chloride, the former must have the constitutional formula, $CH_2Cl—CH_2Cl$, and the third formula for ethylene, $CH_3—CH<$ is thus excluded. The second formula is not probable because, if the existence of free valencies is assumed, they could occur also in non-adjacent carbon atoms, and thus give rise, in the higher hydrocarbons, to numerous isomerides which have, however, never been prepared (if propylene had two free valencies, four isomerides should exist, instead of only one); further, the addition of halogen always takes place at two contiguous carbon atoms (*see* Note on preceding page).

Finally, the assumption of free valencies in organic compounds is inadmissible in view of the unsuccessful attempts to prepare *methylene* (or *methene*), CH_2, for instance, by eliminating HCl from methyl chloride, $2CH_3Cl = 2HCl + 2CH_2<$; the two methylene residues always condense, forming ethylene, as the two valencies cannot remain free.

ETHYLENE, C_2H_4 (Ethene), $H_2C = CH_2$. This is a gas, becoming liquid at −103° and solid at −169°, or liquid at 0° under 44 atmos. pressure. It is very slightly soluble in water or alcohol. It has a somewhat pleasant smell and burns with a luminous flame; indeed, illuminating gas, which contains 2 to 3 per cent. of ethylene, owes part of its luminosity to this gas. When mixed with 2 vols. of chlorine it burns with a dark-red flame, carbon being deposited and HCl formed. At a red heat it yields C, CH_4, C_2H_6, C_2H_2, etc.; with hydrogen in presence of spongy platinum or, better, powdered nickel at 300°, it is converted into ethane.

It is prepared in the laboratory by heating alcohol with excess of sulphuric acid; as an intermediate product, ethylsulphuric acid is formed, this giving ethylene when heated: $C_2H_5 \cdot OH + H_2SO_4 = H_2O + C_2H_5HSO_4$; $C_2H_5HSO_4 = H_2SO_4 + C_2H_4$. Pure ethylene is obtained (1) by passing a mixture of carbon monoxide and hydrogen over finely divided nickel or platinum at 100°: $2CO + 4H_2 = C_2H_4 + 2H_2O$; (2) by dropping alcohol on to phosphoric acid at 200° to 220°; or (3) from ethylene bromide and a copper zinc couple.

PROPYLENE, C_3H_6 (Propene), $CH_2=CH—CH_3$. This may be prepared by heating glycerol with zinc dust or from isopropyl iodide and potassium hydroxide. It is a gas which liquefies at −48° and is isomeric with trimethylene.

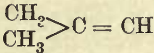
BUTYLENES, C_4H_8 (Butenes). Three isomerides, the α, β, and γ, are known, and are obtained by treating normal, secondary, and tertiary butylene iodides respectively with potassium hydroxide:

$CH_2=CH—CH_2—CH_3$

Butene-1 (α-butylene)

$CH_3—CH=CH—CH_3$

Butene-2 (β-butylene)



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=CH_2$

2-Methylpropene (isobutylene)

Tetramethylene or cylobutane is isomeric with the butylenes.

AMYLENES, C_5H_{10} (Pentenes). Of the various isomerides theoretically possible several have been prepared. By heating *fusel oil* (of distilleries) with zinc chloride, pentanes and various isomeric amylenes are formed which may be separated by means of the different velocities with which HI is added to them, or by the property possessed by some of them of dissolving in the cold in a mixture of concentrated sulphuric acid and water in equal parts, forming amylsulphuric acid, whilst the others either do not react or give condensation products (di- and triamylenes).

NORMAL OCTYLENE or **CAPRYLENE**, C_8H_{16}, is formed as a secondary product in the preparation of *octyl iodide* (from octyl alcohol and phosphorus iodide). It is a colourless liquid, b.-pt. 124°, and with concentrated nitric acid forms nitro- and dinitro-octylene.

CEROTENE, $C_{27}H_{54}$, and **MELENE**, $C_{30}H_{60}$, are similar to paraffin wax, and are obtained by distilling Chinese wax or beeswax.

II. HYDROCARBONS OF THE SERIES, C_nH_{2n-2}

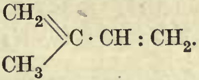
A. With Two Double Linkings (Diolefines or Allenes)

Of the few known terms of this series, the first and best investigated is **ALLENE**, $H_2C:C:CH_2$ (*propandiene*): this is a colourless gas which differs from its isomeride allylene in not forming metallic derivatives; it is obtained by eliminating one atom of bromine from tribromopropane by means of potassium hydroxide and the remaining two by zinc dust, its constitution being thus rendered evident:

$$CH_2Br\cdot CHBr\cdot CH_2Br\rightarrow CH_2:CBr\cdot CH_2BrCH_2:C:CH_2.$$

ERYTHRENE, C_4H_6 (Pyrrolilene or Butan-1 : 3-diene), $CH_2:CH\cdot CH:CH_2$, is a gas found in illuminating gas, and when heated with formic acid gives *erythritol*.

ISOPRENE, C_5H_8, boils at 37° and is obtained by distilling rubber. On the other hand, with concentrated HCl, it condenses, regenerating *rubber* or forming *terpenes*, $C_{10}H_{16}$, $C_{15}H_{24}$, etc. Since *dimethylallene*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C:C:CH_2$, gives, with 2HBr, a dibromide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CBr\cdot CH_2\cdot CH_2\cdot Br$, which is identical with that obtained from isoprene + 2HBr, the constitution of isoprene must be



$\begin{matrix}CH_2\\CH_3\end{matrix}\!>C\cdot CH:CH_2.$

Isoprene was prepared for the manufacture of *synthetic rubber* by decomposing turpentine in various ways, first by Tilden in 1882, and later by Woltereck (1909), Wallace (1909), Harries (1910), and Silberrad (1910: *see* Eng. Pats. 19,701 and 27,908 of 1909, and 4001 of 1910). The Badische Anilin-und Soda-Fabrik (French Pat. 425,885 and Addition No. 14,542, 1911) passes vapours of turpentine or, better, of limonene, dipentene, carvone, etc., over metallic filaments rendered red-hot by the passage of an electric current, the product being diluted either with indifferent gases or by evacuation.

Harries (1910) obtains isoprene by heating halogenated derivatives of isopentane at 600° in presence of basic oxides, carbonates, or organic salts. According to U.S. Pat. 1,206,419 (1912) isoprene (or diolefines in general) is obtained on passing the vapours of dihalogenated paraffins [*e. g.*, trimethylethylene bromide $(CH_3)_2:CBr\cdot CHBr\cdot CH_3$] at 300° into a vacuum over heated barium chloride (catalyst) and washing the resulting vapours in water to fix the HBr.

The normal isomeride, **PIPERYLENE**, $CH_2 : CH \cdot CH_2 \cdot CH : CH_2$ (Pentan-1 : 4-diene) boils at 42° and is obtained from *piperidine.*

DIALLYL, C_6H_{10} (Hexine), is prepared by the general reaction—the action of sodium on allyl iodide—which indicates its constitution :

$$2CH_2 : CH \cdot CH_2I + 2Na = CH_2 : CH \cdot CH_2 \cdot CH_2 \cdot CH : CH_2 + 2NaI.$$

CONYLENE, C_8H_{14} (1 : 4-octadiene), $CH_2 : CH \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH_2 \cdot CH_3$, boils at 126°, and is obtained from *coniine.*

B. Hydrocarbons with Triple Linkings (Acetylene Series)

The most important members of this series are :

Acetylene, C_2H_2 (ethine), $HC \equiv CH$, gas.

Allylene, C_3H_4 (propine), $CH_3 \cdot C \equiv CH$, gas.

Crotonylene, C_4H_6 (2-butine or dimethylacetylene), $CH_3 \cdot C \equiv C \cdot CH_3$, boils at 27°.

Ethylacetylene, C_4H_6 (3-butine), $CH_3 \cdot CH_2 \cdot C \equiv CH$, boils at 18°.

Methylethylacetylene, C_5H_8 (3-pentine), $CH_3 \cdot CH_2 \cdot C \equiv C \cdot CH_3$, boils at 55°.

n-Propylacetylene, C_5H_8 (4-pentine), $CH_3 \cdot CH_2 \cdot CH_2 \cdot C \equiv CH$, boils at 48°.

Isopropylacetylene, C_5H_8 (3-methyl-1-butine), $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH \cdot C \equiv CH$, boils at 28°.

Several of these compounds (the first three) are formed during the dry distillation of coal and other complex substances, and are hence found in lighting gas.

In the laboratory they are obtained by the following methods :

(*a*) By electrolysing acids of the fumaric acid series (*see later*) :

$$COOH \cdot CH \equiv CH \cdot COOH = H_2 + 2CO_2 + HC \equiv CH.$$

(*b*) By heating with alcoholic potash the halogenated compounds (best the bromo-derivatives), $C_nH_{2n}X_2$ and $C_nH_{2n-2}X_2$, gradual elimination of halogen hydracid (of HBr or, in presence of KOH, of KBr and H_2O) occurs :

$$C_2H_4Br_2 = HBr + C_2H_3Br \longrightarrow HBr + C_2H_2.$$

In general, starting from the saturated hydrocarbons, C_nH_{2n+2}, *the action of halogen and elimination of halogen hydracid gives an unsaturated hydrocarbon,* C_nH_{2n}; *addition of halogen to this and subsequent removal of halogen hydracid gives a still less saturated hydrocarbon,* C_nH_{2n-2}, *and so on.*

Elimination of 2HCl from the compounds $C_nH_{2n}Cl_2$, obtained from aldehydes or from certain ketones (methylketones, $C_nH_{2n+1} \cdot CO \cdot CH_3$) by the action of PCl_5, yields always a trebly linked compound, in which, however, one of the carbon atoms is always united to a single, characteristic hydrogen atom : $-C \equiv CH$; for example, acetaldehyde gives ethylidene chloride, $CH_3 \cdot CHCl_2$, which then yields $2HCl + CH \equiv CH$; while acetone, $CH_3 \cdot CO \cdot CH_3$, gives chloroacetone, $CH_3 \cdot CCl_2 \cdot CH_3$, and this $2HCl + CH_3 \cdot C \equiv CH$, the elimination of halogen hydracid never occurring in such a way as to give compounds with two double linkings, such as $CH_2 : C : CH_2$.

Acetylene derivatives are obtained also by heating the acids of the propiolic series (*see later*).

Compounds with this characteristic hydrogen atom $-C \equiv CH$ have a feebly acid character and form solid metallic derivatives (*acetylides*) when treated with an ammoniacal solution of copper chloride or silver nitrate : *copper acetylide*, $Cu \cdot C \equiv C \cdot Cu, H_2O$, having a reddish-brown colour and apparently the constitution $Cu_2CH \cdot CHO$, since with hydrogen peroxide it gives *acetaldehyde*, $CH_3 \cdot CHO$ (Makowka, 1908); and *silver acetylide*, $AgC \equiv CAg$, which is white and insoluble in water or ammonia and, in the dry state, is extremely explosive, simple rubbing being sufficient to explode it. With hydrochloric acid it regenerates acetylene in a pure state.

The proof that it is the characteristic hydrogen atom which is replaced by metals lies in the fact that acetylene derivatives from other ketones (not from methylketones) do not give metallic acetylides :

$$CH_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3 \rightarrow CH_3 \cdot CH_2 \cdot CCl_2 \cdot CH_2 \cdot CH_3 \longrightarrow$$
$$2HCl + CH_3 \cdot C \vdots C \cdot CH_2 \cdot CH_3.$$

Four atoms of a halogen or of hydrogen may be added to the hydrocarbons of the acetylene series, saturated compounds being formed ; as a rule, however, only two atoms are readily added, although under the action of light four halogen atoms may be added almost always.

The compounds of the olefine series may, however, be distinguished from those of the acetylene series by means of the *ozone reaction*, since compounds with a triple linking do not fix ozone from ozonised air at all (Molinari ; *see* p. 107).

The hydrocarbons of the acetylene series take up a molecule of water in presence of mercury salts, giving rise to complex mercuric compounds, which, with HCl, give as final product an aldehyde or ketone of the saturated series : $CH_3 \cdot C \vdots CH$ (allylene) $+ H_2O = CH_3 \cdot CO \cdot CH_3$ (acetone) or $CH \vdots CH + H_2O = CH_3 \cdot CHO$ (acetaldehyde). The last reaction serves to illustrate the transformation of inorganic into organic substances (*see later*, chapter on Alcohol).

In the acetylene series, also, condensation or polymerisation is possible, three molecules of acetylene, when heated, yielding benzene, C_6H_6 ; three molecules of dimethylacetylene, C_4H_6, giving, with concentrated sulphuric acid, *hexamethylbenzene*, $C_6(CH_3)_6$, and allylene, C_3H_4, similarly yielding *trimethylbenzene* (*mesitylene*), $C_6H_3(CH_3)_3$.

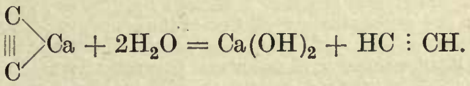
In the higher compounds, the position of the triple bond is deduced from the oxidation products, since, as with substances with a double linking, the breaking of the chain occurs at the multiple linking.

When certain acetylene derivatives, *e. g.*, $XC \equiv C \cdot CH_3$, are heated with sodium, the triple bond changes its position, the products being sodium derivatives of isomeric hydrocarbons, $X \cdot CH_2 \cdot C \vdots CH$ (these give metallic acetylides, but the original compounds do not) ; when these are heated with alcoholic potash, the reverse change occurs.

ACETYLENE, C_2H_2 (Ethine), $HC \vdots CH$. Without having isolated or characterised this compound, Davy obtained it in 1839 in a very impure condition, by treating with water the product obtained by heating together potassium carbonate and carbon, which should yield potassium. Berthelot first obtained it pure (and named it) in 1859, by passing ethylene or alcohol or ether vapour through a red-hot tube ; he prepared it also by means of a voltaic arc passing between two carbons in an atmosphere of hydrogen. In 1862, Wöhler prepared it by treating calcium carbide (obtained by heating carbon with an alloy of zinc and calcium) with water.

It is formed in the incomplete combustion of various hydrocarbons and of illuminating gas (*e. g.*, in the flame of a bunsen burner alight at the bottom).

The industrial preparation of acetylene has assumed great and unforeseen practical importance since 1870, when it became possible to prepare *calcium carbide* on an enormous industrial scale by means of the electric furnace (*see* "Calcium Carbide Industry," Vol. I., p. 638) :



$$\overset{C}{\underset{C}{|||}} \!>\! Ca + 2H_2O = Ca(OH)_2 + HC \vdots CH.$$

Acetylene is a colourless gas, sp. gr. 0·92 (1 litre weighs 1·165 grams), with a pleasant odour when pure and a disagreeable one when impure (as usually obtained). At + 1° under a pressure of 48 atmos. it forms a highly refractive, mobile, colourless liquid, sp. gr. 0·451, and, on evaporating rapidly, partially solidifies in the form of snow, m.-pt. −81°.

One volume of acetylene gas dissolves in 1·1 vols. of water, or in $\frac{1}{6}$ vol. of alcohol or in 20 vols. of saturated salt solution; 1 litre of acetone dissolves 24 litres of acetylene, or 300 litres at 12 atmos., or about 2000 litres at −80°, its volume being then increased fourfold. Permanganate oxidises it, giving oxalic acid, and chromic acid acetic acid.

It is an endothermic compound, requiring for its formation from its elements, 61,000 cals.; it is hence very unstable and is readily decomposed by the detonation of a mercury fulminate cap or by an electric discharge, developing as much heat as an equal volume of hydrogen on conversion into water. The explosion takes place much more readily and is much more dangerous with the compressed gas and still more so with the liquid.

Acetylene decomposes at 780° and, when mixed with air, ignites at 480°. One cubic metre (1·165 kilos) of acetylene, in burning, develops 14,350 Cals. (12,300 Cals. per kilo), whilst ordinary coal-gas gives about 5000 Cals.

When mixed with air or, better, with oxygen it forms a *detonating mixture* which explodes with great energy in contact with an ignited body. The explosion is violent even with 1 vol. of acetylene and 40 vols. of air; it reaches its maximum violence with 1 vol. of the gas and 12 vols. of air (2·5 vols. of oxygen), whilst scarcely any explosion but mere burning takes place with 1 vol. of acetylene and 1·3 vols. of air (as has been already stated on p. 34, ordinary illuminating gas only explodes when at least 1 vol. is present to about 20 vols. of air).

Explosive mixtures of acetylene are more dangerous than those of coal-gas owing to the greater speed of propagation of the explosion (*e. g.*, with 1 vol. of acetylene and 40 of air), the explosive force being thus increased (*see* section on Explosives); further, acetylene contains less hydrogen and hence forms less water, the condensation of the gases resulting from the explosion being consequently smaller. The wide limits of the explosive mixtures (from 2·4 to 130 vols. of acetylene per 100 vols. of air) are explained by the fact that this gas, being an endothermic compound, reacts or decomposes with great facility.

In contact with copper, bronze, silver, etc., acetylene readily forms explosive acetylides (*see* p. 110),[1] but when perfectly dry does not attack metals.

It was at first thought that acetylene, like carbon monoxide, was poisonous, but experiments made during the last few years have shown that animals do not die in an atmosphere containing 9 per cent. or, in some cases, even 20 per cent. of the gas. When, however, the acetylene is highly contaminated with sulphides and phosphides, it may be poisonous.

With an ordinary gas-jet, acetylene burns with a reddish, smoky flame, but by passing the gas at a pressure of 60 mm. through two jets nearly meeting at an angle, a white, highly luminous, fan-shaped flame is obtained without the dark middle portion of the ordinary bat's-wing coal-gas flame.

One kilo of chemically pure calcium carbide should yield theoretically 349 litres of acetylene, and good commercial carbide yields practically 300 litres. The luminosity of

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[1] The ready formation of metallic acetylides, especially that of copper, led Erdmann (1907) to devise a rapid and exact analytical method for the direct quantitative precipitation of copper from any solution and in presence of any metals (except Ag, Hg, Au, Pd, and Os, which must be previously eliminated): the feebly alkaline solution of the copper salt is reduced until decolorised with hydroxylamine hydrochloride, C_2H_2 being then passed through and the precipitated copper acetylide collected on a filter, washed with water and pumped off; together with the filter-paper it is introduced into a porcelain crucible, treated with 10 to 15 c.c. of dilute nitric acid (sp. gr. 1·15) and eight to ten drops of concentrated nitric acid (sp. gr. 1·52), dried on a water-bath, heated rapidly to redness and weighed as CuO. The acetylene used for this precipitation should be washed with lead acetate solution.

acetylene in comparison with that of other substances has already been referred to on p. 64. A proportion of 2 vols. of air to 3 of acetylene gives the maximum luminosity, and at the present time special incandescent mantles are made for use with acetylene.

The impurities present in ordinary acetylene (98 to 99 per cent. purity) are: N, NH_3, CO, H_2S, and PH_3, the last three of which are poisonous. The gas is purified by passing it through an *acid* solution of a metallic salt.

Lunge and Cederkreutz recommend chloride of lime (hypochlorite) for purifying acetylene, care being taken that the mass does not heat, as this would be dangerous. Latterly it has been suggested to fix the PH_3 by passing the gas through concentrated sulphuric acid (64° Bé.) saturated with As_2O_3. A good purifying material is made by preparing a paste of calcium hypochlorite, quicklime, sodium silicate, and powdered calcium carbide, this remaining porous when allowed to dry in the air.

USES. When the great calcium carbide industry was started, it appeared as though acetylene would be used solely as a competitor of illuminating gas, electricity, petroleum, etc., but most of the acetylene is now employed in cutting metals, while calcium carbide is largely used for the manufacture of calcium cyanamide (*see* Vol. I., p. 371).

The use of liquid acetylene would be very convenient, but is highly dangerous, since a sharp blow or other accident might easily produce a terrible explosion.

It is still too expensive to employ in place of benzene for carburetting coal-gas. Dissolved in acetone (Claude and Hess, 1896), which dissolves a large quantity of it (*vide infra*), it is used to great advantage for the *oxy-acetylene blowpipe* in place of oxy-hydrogen. With the latter, for every cubic metre of oxygen 4 cu. metres of hydrogen are used practically (theoretically 2 cu. metres), whilst the same amount of oxygen burns with 600 litres of acetylene (theoretically 400 litres), which costs much less than 4 cu. metres of hydrogen. The oxy-acetylene flame exhibits at the centre a shining point, which has a temperature of 2800° to 3000°, and to weld iron sheets 1 mm. thick requires 50 to 75 litres of acetylene per hour, 5 metres being welded in this time.

With a slight excess of oxygen large tubes are easily cut and steel blocks perforated.

Acetylene dissolved in acetone, especially if the solution is ab orbed by porous material, is not at all dangerous and may be transported in iron cylinders.

In moderate quantities acetylene dissolved in acetone is sold compressed in iron bottles capable of yielding 650 litres of the gas; these bottles are convenient for lighting mines, railway carriages, automobiles, etc. In the United States 300,000 of such bottles were used in 1913, while in Germany 6000 were used for automobiles alone.

Acetylene is utilised in the preparation of numerous chloro-derivatives which have various practical applications, *e. g.*, in the manufacture of indigo, acetaldehyde, acetic acid, and alcohol (*see below*). It is used also in the synthesis of thiophene (Steinkopf's method: *see* chapter on Thiophene), and also in that of rubber (according to Heinemann); when heated, a mixture of acetylene and ethylene condenses to *butandiene*, $CH_2:CH\cdot CH:CH_2$, this being converted by methylation into *isoprene*, $CH_2:C(CH_3)\cdot CH:CH_2$, which is polymerised by concentrated hydrochloric acid with formation of *synthetic rubber.*

By repeated passage of a mixture in equal volumes of acetylene and hydrogen through tubes heated electrically to 650° to 800°, considerable polymerisation of the acetylene is effected with formation of about 60 per cent. of tar containing 20 per cent. of benzene, a certain amount of naphthalene, and a little toluene, anthracene, diphenyl, fluorene, etc. (R. Meyer, 1912).

Large quantities of acetylene are decomposed by the electric discharge to make very pure hydrogen and lamp-black (*see* Vol. I., pp. 142, 458; *also* R. P. Pictet's Ger. Pat. 255,733, 1909).

The hope of manufacturing synthetic alcohol economically from acetylene had died out, but during the European War the enormous rise in the price of alcohol turned attention to this synthesis, although the industrial experiments which followed could not be sustained in normal times (*see later:* Alcohol).

Even for engines it is still too dear to use. Acetylene can, however, be used conveniently with a rational plant and relatively small gasometers connected with iron tubes which carry the gas direct to the burners (when prepared from pure carbide), but it is necessary to avoid the use of copper or bronze in any part of the gasometers, pipes, and taps, in order to avoid explosions, which are almost always due to the formation of copper acetylide.[1]

In testing the purity of acetylene the only quantitative determination usually made is that of the hydrogen phosphide, which should not occur in greater proportion than 1 gram per cubic metre, since, besides being poisonous and having an unpleasant smell, it facilitates the formation of explosive metallic acetylides. (The estimation of the impurities in carbide is described in Vol. I., p. 639.)

III. HYDROCARBONS OF THE SERIES, C_nH_{2n-4} and C_nH_{2n-6}

DIACETYLENE, C_4H_2 (Butandiine), $CH \vdots C \cdot C \vdots CH$, is a gas and forms the usual metallic acetylides.

DIPROPARGYL, C_6H_6 (Hexan-1 : 5-diine), $CH \vdots C \cdot CH_2 \cdot CH_2 \cdot C \vdots CH$, is isomeric with benzene, boils at 85°, and can take up 8 atoms of bromine. It is obtained from diallyl, C_6H_{10}, and readily forms metallic acetylides.

HEXAN-2 : 4-DIINE, $CH_3 \cdot C \vdots C \cdot C \vdots C \cdot CH_3$, is also isomeric with benzene.

BB. HALOGEN DERIVATIVES OF THE HYDROCARBONS

The Table on page 115 summarises the physical properties of the more important halogen derivatives of the hydrocarbons, the first column giving the hydrocarbon *residue* (*alkyl*) united with the halogen.

I. HALOGEN DERIVATIVES OF SATURATED HYDROCARBONS

PROPERTIES. Very few are gases, several are liquids, and those which contain many atoms in the molecule are solids. The iodo-compounds boil at higher temperatures than the corresponding bromo- and chloro-compounds. They are very slightly, if at all, soluble in water, but are readily soluble in alcohol, ether, and glacial acetic acid.

Most of them burn easily, and ethyl and methyl chlorides colour the edges of the flame green. Some of them, containing few carbon atoms, produce *anæsthesia, e. g.*, $CHCl_3$, CH_2Cl_2, $C_2H_3Cl_3$, C_2H_5Br, C_2H_5Cl.

Generally they do not react with silver nitrate, since these compounds are not dissociated in solution, and do not give free halogen ions (*see* Vol. I., pp. 96, 98 *et seq.*). In alcoholic solution, ethyl iodide gives a little precipitate in the cold, and ethyl bromide in the hot, whilst the chloride gives no precipitate at all, with silver nitrate.

The bromo- and iodo-compounds exhibit great reactivity and effect the most varied and interesting reactions and syntheses; methyl iodide reacts the most readily of all, the reactivity diminishing with increase of molecular weight.

The halogens of these compounds may easily be replaced by H (by sodium-amalgam, or zinc dust and hydrochloric or acetic acid).

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[1] The numerous types of apparatus for generating acetylene may be divided into three groups :

(1) Those where the carbide and water are in separate vessels communicating by a tube furnished with a tap which automatically opens more or less and so diminishes or increases the supply of the gas. To prevent the carbide, or rather the lime formed, from holding water and generating gas even after the tap is closed, the carbide is impregnated with an indifferent substance, *e. g.*, paraffin wax, stearine, oil, sugar (to dissolve the lime as calcium saccharate), etc. One inconvenience of this procedure is that at some places the carbide, in presence of little water, becomes excessively heated and may produce an explosion, which is dangerous if the gas is under pressure.

(2) Those where the carbide is suspended at a certain part of the vessel containing the water; acetylene is then generated when the level of the water rises to the carbide and ceases automatically when it falls.

(3) Those where the carbide and water are separated, a small quantity of carbide being dropped into excess of water. This would be the most rational method, but is perhaps not the most convenient owing to the difficulty of powdering the carbide (often very hard) without allowing it to absorb moisture.

These derivatives may, to some extent, be transformed one into the other, *e. g.*, the chlorides into iodides by treatment with KI or CaI_2, and the iodides into the fluorides (more volatile than the chlorides) by means of silver fluoride.

Alkyl	Names of the Alkyls and Isomerides	Chlorides		Bromides		Iodides	
		B.-pt.	Sp. gr.	B.-pt.	Sp. gr.	B.-pt.	Sp. gr.
	a SATURATED DERIVATIVES						
	(1) *Monosubstituted*						
CH_3	Methyl	− 23·7°	0·952 (0°)	+ 4·5°	1·732 (0°)	+ 45°	2·293 (18°)
C_2H_5	Ethyl	+ 12·2°	0·918 (0°)	38·4°	1·468 (13°)	+ 72·3°	1·944 (14°)
C_3H_7	n-Propyl	+ 46·5°	0·912 (0°)	71°	1·383 (0°)	102·5°	1·786 (0°)
	Isopropyl	36·5°	0·882 (0°)	60°	1·340 (0°)	89°	1·744 (0°)
C_4H_9	n-Butyl (primary)	78°	0·907 (0°)	101°	1·305 (0°)	130°	1·643 (0°)
	Isobutyl	68·5°	0·895 (0°)	92°	1·204 (16°)	119°	1·640 (0°)
	sec.-Butyl	—	—	—	—	119–120°	1·626 (0°)
	tert.-Butyl	55°	0·866 (0°)	72°	1·215 (20°)	100°	1·571 (0°)
C_5H_{11}	n-Amyl (primary)	107°	0·901 (0°)	129°	1·246 (0°)	156°	1·543 (0°)
	Isoamyl, $(CH_3)_2 : CH \cdot CH_2 \cdot CH_2 \cdot X$	101°	0·893 (0°)	121°	1·236 (0°)	148°	1·468 (0°)
	tertiary-Butylmethyl $(CH_3)_3(C \cdot CH_2 \cdot X$	—	0·879 (0°)	—	1·225 (0°)	—	1·050 ? (0°)
	active-Amyl $(CH_2)(C_2H_5)CH \cdot CH_2 \cdot X$	97·99°	0·886 (15°)	118–120°	1·221 (20°)	148°	1·524 (20°)
C_6H_{13}	n-Hexyl (primary)	134°	0·892 (16°)	156°	1·193 (0°)	182°	1·461 (0°)
	n-Hexyl (secondary)	—	—	144°	—	168°	1·453 (0°)
C_7H_{15}	n-Heptyl (primary)	159°	0·881 (16°)	179°	1·113 (16°)	201°	1·386 (16°)
C_8H_{17}	n-Octyl (primary)	180°	0·880 (16°)	199°	1·116 (16°)	221°	1·345 (16°)
	(2) *Disubstituted*						
$>CH_2$	Methylene, CH_2X_2	42°	—	97°	—	180°	—
$-CH_2 \cdot CH_2-$	Ethylene	84°	—	131°	—	—	—
$CH_3 \cdot CH_2 <$	Ethylidene (or ethydene)	57°	—	108°	—	—	—
	(3) *Trisubstituted*						
	CHX_3 (chloroform, bromoform, iodoform)	61°	—	151°	—	solid m.-pt. 119°	—
	$CH_3 \cdot CCl_3$ methylchloroform (*a*-trichloroethane)	74°	—	188°	—	—	—
	$CH_2Cl \cdot CHCl_2$ (β-trichloroethane)	114°	—	220°	—	—	—
	$CH_2X \cdot CHX \cdot CH_2X$ (trichlorohydrin, tribromohydrin)	158°	—	—	—	—	—
	(4) *Polysubstituted*						
	CX_4 (carbon tetrachloride, iodide)	77°	—	—	—	solid	—
	C_2Cl_6 perchloroethane	solid m.-pt. 187°	—	—	—	—	—
	(*b*) UNSATURATED DERIVATIVES						
	(1) *Ethylenic series*						
$CH_2 : CH \cdot X$	Vinyl chloride, etc.	− 18°	—	23°	—	56°	—
$C_3H_5 \cdot X$	Allyl ,,	46°	—	70°	—	101°	—
$C_2H_2 : X_2$	Dichloroethylene	55°	—	—	—	—	—
$C_2H \vdots X_3$	Trichloroethylene	88°	—	—	—	—	—
$C_2 \vdots X_4$	Tetrachloroethylene	121°	—	—	—	—	—
	(2) *Acetylene series*						
$HC \vdots CX$	Monochloro- and monobromo-acetylene	gas	—	gas	—	—	—

METHODS OF PREPARATION. (*a*) By the action of halogens on saturated hydrocarbons: chlorine and bromine react directly at the ordinary temperature on the gaseous hydrocarbons, and on heating with the liquid ones.

The first halogen atom is fixed more readily than the succeeding ones, and the addition of iodine facilitates the reaction with bromine and chlorine, since the iodine forms, for example, ICl_3, which readily gives nascent chlorine, $ICl_3 = ICl + Cl_2$ (*i. e.*, it acts like $SbCl_5$, which yields $SbCl_3 + Cl_2$). By saturating with chlorine and heating under pressure energetic chlorinations may be affected.

Methane, ethane, propane, etc., exchange their hydrogen atoms one by one for chlorine atoms, the completely substituted compounds (C_2Cl_6, C_3Cl_8, etc., and especially the higher ones), on further energetic chlorination, being resolved into other completely chlorinated compounds containing less numbers of carbon atoms: $C_2Cl_6 + Cl_2 = 2CCl_4$; $C_3Cl_8 + Cl_2 = C_2Cl_6 + CCl_4$, a little hexachlorobenzene, etc., being always formed as well.

Iodine scarcely ever acts directly on the hydrocarbons, since the HI formed acts in the opposite sense on the iodo-products. The reaction proceeds only in presence of iodic acid or mercuric oxide, which fixes the hydriodic acid as it is formed.

The iodo-compounds are easily obtained from zinc-alkyls and iodine.

When the halogens act directly, the more energetic (F or Cl) replaces the weaker (Br or I). The iodo-compounds may, however, be easily obtained by first preparing the magnesium compounds of the alkyl chlorides or bromides and treating these with iodine:

$$\text{Alkyl–Mg–Cl} + I_2 = \text{Alkyl–I} + \text{MgICl}.$$

(*b*) *Unsaturated hydrocarbons*, with the halogen hydracids, give saturated monosubstituted derivatives: $C_2H_4 + HBr = C_2H_5Br$, ethyl bromide, etc.; if the halogens act directly, disubstituted saturated products are obtained: $C_2H_4 + Cl_2 = C_2H_4Cl_2$, ethylene dichloride.

Propylene, $CH_3 \cdot CH : CH_2$, reacts with HI, giving *isopropyl iodide*, $CH_3 \cdot CHI \cdot CH_3$, which is decomposed by alcoholic potash, yielding propylene; *normal propyl iodide*, $CH_3 \cdot CH_2 \cdot CH_2I$, which also yields propylene when HI is removed from it, may thus be converted into isopropyl iodide.

Similar behaviour is exhibited by the butyl iodides.

The halogen always goes to the carbon atom united with the lesser number of hydrogen atoms: $CH_3 \cdot CH : CH_2 + HI = CH_3 \cdot CHI \cdot CH_3$.

(*c*) The *alcohols*, $C_nH_{2n+1}OH$, with the halogen hydracids give: $C_nH_{2n+1}OH + HBr = H_2O + C_nH_{2n+1}Br$, but the reverse action also proceeds, and to limit this, excess of the halogen hydracid is used and the water formed is fixed, *e. g.*, by addition of zinc chloride.

Further, the chlorine of the phosphorus chlorides also replaces hydroxyl: $PCl_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5Cl$, or, better, $PCl_5 + C_2H_5OH = POCl_3 + HCl + C_2H_5Cl$. This reaction is of importance for the preparation of the bromo- and iodo-compounds: $3CH_3 \cdot OH + P + 3I = 3CH_3I + H_3PO_3$; the bromine or iodine first acts on the phosphorus to form PBr_3 or PI_3, this then reacting with the alcohol.

The polyhydric alcohols act in the same way; for example, glycerol, $C_3H_5(OH)_3$, reacts with PCl_5, giving trichlorohydrin, $CH_2Cl \cdot CHCl \cdot CH_2Cl$.

The resulting halogenated products are easily separated by distillation, as the phosphorous acid does not distil. In these, as in most other chemical reactions, secondary products are always formed; these are often very complex, and form viscous resins of unknown composition.

(*d*) The *aldehydes* and *ketones* yield disubstituted products: for example, ethylidene chloride, $CH_3 \cdot CHCl_2$, is obtained from acetaldehyde, $CH_3 \cdot CHO$, and dichloropropane, $CH_3 \cdot CCl_2 \cdot CH_3$, from acetone, $CH_3 \cdot CO \cdot CH_3$, by the action of PCl_5.

METHYL CHLORIDE (Chloromethane), CH_3Cl. This is prepared by passing hydrogen chloride into boiling methyl alcohol containing half its weight of zinc chloride in solution, or by heating 1 part of methyl alcohol with 3 parts of concentrated sulphuric acid and 2 parts of concentrated hydrochloric acid. Industrially it may be obtained by heating methyl alcohol and crude, concentrated hydrochloric acid together in an autoclave, the mass issuing from the hot autoclave as gas being washed with water and concentrated hydrochloric acid and the residual dry chloromethane liquefied by cooling at the pressure of the autoclave itself. Douane (U.S. Pat. 777,406) suggested an apparatus for continuous manufacture.

It is also obtained to-day in appreciable quantity, by the old Vincent process, from the final residues of the beet-sugar industry, which are evaporated and then dry-distilled. In this way an abundant quantity of trimethylamine is formed; this is neutralised with HCl, and the hydrochloride distilled at 300°. A regular evolution of methyl chloride and trimethylamine is thus obtained:

$$\underset{\text{Trimethylamine hydrochloride}}{3N(CH_3)_3HCl} = 2CH_3Cl + \underset{\text{Trimethylamine}}{2N(CH_3)_3} + \underset{\text{Methylamine hydrochloride (residue)}}{CH_3 \cdot NH_2,\ HCl}.$$

The chloromethane, distilled as a gas, is purified with HCl, dried with $CaCl_2$, and liquefied in steel cylinders under pressure, just as is done with carbon dioxide (Vol. I., p. 480).

It is a colourless gas of ethereal odour, and at —24·09° becomes liquid, then having the sp. gr. 0·952 (at 0°). Water dissolves one-fourth of its volume, and alcohol rather more. It burns with a green-edged flame.

In the liquefied condition it is used as a local anæsthetic; it is used also to extract perfumes from flowers, and in considerable quantities for the manufacture of dyestuffs (methyl green), especially for methylation, but the greatest amount is employed in cooling machines. In France there are about 100 ice-machines which use methyl chloride instead of liquefied NH_3, CO_2, or SO_2. In brass cylinders containing from 1 to 30 kilos it is sold at 11*s.* to 14*s.* 6*d.* per kilo, in addition to the cost of the cylinder, which is 20*s.* for the 1-kilo, 25*s.* 6*d.* for the 3-kilo, and £3 16*s.* for the 30-kilo size.

METHYL IODIDE, CH_3I, is prepared from methyl alcohol, phosphorus, and iodine as described later for ethyl iodide. It is a liquid of sp. gr. 2·293, boiling at 45°; with excess of water at 100° it is decomposed into hydrogen iodide and methyl alcohol.

ETHYL CHLORIDE (Chloroethane), C_2H_5Cl, was termed by Basil Valentine "Spiritus salis et vini," or *spirit of sweet wine.* It is obtained from ethane and chlorine, or by passing hydrogen chloride into a solution of zinc chloride and ethyl alcohol. It is formed also as a secondary product in the manufacture of chloral. It boils at + 12·2° and burns with a flame having green edges. It is a local anæsthetic and is soluble in alcohol, but only slightly so in water. It costs from 1*s.* 7*d.* to 4*s.* per kilo in metal cylinders containing 1 to 30 kilos.

ETHYL IODIDE, C_2H_5I, is prepared by digesting 10 grams of red phosphorus with 80 grams of absolute alcohol for twelve hours and gradually adding 100 grams of iodine; the mixture is then heated for two hours under a reflux condenser and the ethyl iodide distilled on the water-bath, washed with dilute alkali and with water, and dried by means of calcium chloride. When yellow instead of red phosphorus is used, much less of it is required and the reaction is more rapid, boiling being unnecessary; yellow phosphorus is, however, inconvenient to work with. From 3 to 4 kilos of ethyl iodide are obtained from 3 kilos of iodine. According to Ger. Pat. 175,209, ethyl iodide is obtained quantitatively if diethyl sulphate is slowly added to the calculated amount of hot potassium iodide solution. It boils at 72·3° and has the sp. gr. 1·944 (at 14°); it is highly refractive and dissolves in alcohol or ether. It decomposes when heated with water at 100°. Chlorine converts it into ethyl chloride and bromine into ethyl bromide. In the light it slowly decomposes with separation of iodine, which colours the liquid brown, but it remains colourless in presence of a drop of mercury. It is used as an inhalation for the treatment of asthma. It costs about 28*s.* to 32*s.* per kilo.

ETHYL FLUORIDE, C_2H_5F, is liquid at —48°, burns with a blue flame, and does not attack glass.

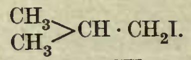
From **PROPANE** two series of isomeric compounds are derived: $CH_3 \cdot CH_2 \cdot CH_2X$, prepared from normal propyl alcohol, and $CH_3 \cdot CHX \cdot CH_3$, derived from isopropyl alcohol, and hence from acetone.

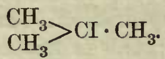
ISOPROPYL IODIDE (Iodo-2-propane) $CH_3 \cdot CHI \cdot CH_3$, is obtained from glycerol, phosphorus and iodine, small amounts of allyl iodide and propylene being also formed.

The butyl compounds occur in four isomeric modifications:

NORMAL BUTYL IODIDE (Iodo-1-butane), $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$.

SECONDARY BUTYL IODIDE (Iodo-2-butane), $CH_3 \cdot CH_2 \cdot CHI \cdot CH_3$.

ISOBUTYL IODIDE (Methyl-2-iodo-3-propane),  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2I$.

TERTIARY BUTYL IODIDE (Methyl-2-iodo-2-propane),  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CI\cdot CH_3$.

The constitutions of the four isomerides are deduced from those of the corresponding butyl alcohols, from which they are obtained by the action of hydriodic acid.

Of the **AMYL** derivatives eight isomerides are known.

METHYLENE CHLORIDE (Dichloromethane), CH_2Cl_2, *bromide* and *iodide* (*see* Table, p. 115).

ETHYLENE COMPOUNDS, $CH_2X\cdot CH_2X$, are formed from ethylene by the addition of halogens or from glycol, $C_2H_4(OH)_2$ and halogen hydracids.

ETHYLIDENE (or Ethydene) **COMPOUNDS**, $CH_2\cdot CHX_2$, are obtained by substituting the oxygen of the aldehydes by halogens.

ETHYLENE CHLORIDE (Dichloro-1 : 2-ethane), $CH_2Cl\cdot CH_2Cl$ (*Dutch liquid*, 1795) boils at 84°. The **IODIDE, BROMIDE,** and **CHLORIDE** with alcoholic potash give acetylene and glycol.

ETHYLIDENE CHLORIDE (Ethydene chloride or Dichloro-1 : 1-ethane), $CH_3\cdot CHCl_2$, is obtained from aldehyde and phosgene : $CH_3\cdot CHO + COCl_2 = CO_2 + CH_3\cdot CHCl_2$, chloral (*which see*) being also formed; it boils at 57°.

CHLOROFORM (Trichloromethane), $CHCl_3$. Chloroform was discovered by Liebig and Souberain and its constitution shown by Dumas in 1835.

It is a colourless liquid with a sweet ethereal smell and taste; it dissolves only to a slight extent in water (0·7 per cent.), but is soluble in alcohol or ether. It boils at 61·2°, and its vapour pressure at 20° is 160 mm. of mercury; its specific gravity is 1·5263 at 0° and 1·500 at 15°, referred to water at 4°.

It is non-inflammable, and it dissolves resins, rubber, fats, and iodine, with the last of which it gives violet solutions.

Chromic acid transforms chloroform into *phosgene* ($COCl_2$), while potassium amalgam gives acetylene. With potassium hydroxide it gives potassium formate and chloride :

$$CHCl_3 + 4KOH = 3KCl + H\cdot CO_2K + 2H_2O.$$

With ammonia at a red heat it gives hydrocyanic and hydrochloric acids :

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

Exposed to light and air, it decomposes partially into Cl, HCl, and $COCl_2$, but it can be kept in yellow bottles, while that for pharmaceutical use keeps better if 1 per cent. of absolute alcohol is added. The presence in it of more than 1 per cent. of alcohol is shown by shaking the chloroform in a test-tube with a granule of pure permanganate, a yellowish-brown spot forming round the latter and also on the glass where it rests.

It is the most efficacious *anæsthetic* (Simpson, 1848), but in some cases may cause death if not used with great care, since it acts on the heart; to diminish this effect, it is mixed with atropine or morphine.[1] The harmful

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[1] From coal-tar products various *anæsthetics* or *hypnotics* are produced synthetically, and these have been of great service to medicine, especially to surgery, rendering possible the execution of the most complicated operations without any pain to the patient. At first substances were used which produced *general anæsthesia* of the organism, but they were accompanied by many inconveniences, sometimes by fatal results.

Indeed, the anæsthetic is transported by the blood into contact with the higher nervous centres by which pain is felt, producing poisoning and paralysis of them, often lasting for some time; at the same time an influence is felt by the centres controlling the action of the heart and of respiration, this being the cause of the danger and disturbance produced by general anæsthesia. The nerve-currents start from the periphery, from the points where the surgical operation is to begin, and are transmitted to the brain, which transforms them into painful sensations, and it is by influencing the cerebral centres by anæsthetics that pain is avoided; anæsthesia ceases, however, to be dangerous if the peripheral nervous centres at the beginning of the nerve-currents are paralysed without the latter reaching the brain. Thus *local anæsthesia* is much more rational effects of chloroform are due sometimes to its decomposition products, especially to phosgene, $COCl_2$.

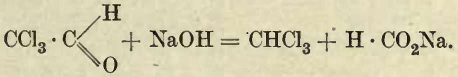
The use of chloroform has been suggested to render pigs insensible, so as to kill them painlessly and to skin them more easily. Also, in fattening them, they are subjected to periodic inhalations of chloroform, which renders them more restful.

Chloroform is sometimes used for dissolving rubber and gutta-percha, for extracting alkaloids and ethereal oils, and, together with acetone and alkali, for preparing *acetone-chloroform* or *chloretone*, which has a slight camphor-like odour, melts at 80° to 81°, and serves as a hypnotic, as a local anæsthetic and as an antiseptic.

PREPARATION. It is prepared from (1) ethyl alcohol or (2) acetone, by heating with chloride of lime and water. In the former case there is always an appreciable evolution of CO_2, which originates in the oxidation of the alcohol, and liberates HClO and so forms aldehyde and hence chloral, $CCl_3 \cdot CHO$, this, in presence of lime, yielding chloroform and calcium formate: $2CCl_3 \cdot CHO + Ca(OH)_2 = 2CHCl_3 + Ca(HCO_2)_2$. If the decomposition of the hypochlorite is rapid, evolution of oxygen may occur.

The reaction taking place in the industrial process is perhaps best interpreted by the equation: $4C_2H_5 \cdot OH + 16CaOCl_2 = 3Ca(HCO_2)_2 + 13CaCl_2 + 8H_2O + 2CHCl_3$. With acetone the reaction would be as follows, trichloroacetone being formed as an intermediate product: $2CH_3 \cdot CO \cdot CH_3 + 6CaOCl_2 = Ca(C_2H_3O_2)_2$ (calcium acetate) $+ 2CHCl_3 + 3CaCl_2 + 2Ca(OH)_2$.

In a very pure form for pharmaceutical use it is obtained by treating chloral with aqueous caustic soda solution, sodium formate being also formed:



$$CCl_3 \cdot C\begin{matrix}\diagup H \\ \diagdown O\end{matrix} + NaOH = CHCl_3 + H \cdot CO_2Na.$$

To obtain very pure chloroform from the impure product, Anschütz treats the latter with salicylic anhydride, $C_6H_4CO_2$, which forms a crystalline mass only with chloroform, $(C_6H_4CO_2)_4, 2CHCl_3$; this, after separation from the mother-liquor, is heated on the water-bath, when pure chloroform distils off.

Pictet Chloroform is pure chloroform obtained from the commercial product by freezing it at − 80° to − 120°; the impurities remain in the liquid, the crystals giving pure chloroform.

INDUSTRIAL PREPARATION. A considerable amount of chloroform is prepared even to-day from chloride of lime and alcohol, but the latter should not contain fusel oil.

In America, F. W. Frericks suggests the arrangement shown in Fig. 104 for the manufacture of chloroform. In the boiler *B* 550 litres of 94 per cent. alcohol and 2550 litres of water (giving 20 per cent.of alcohol in the mixture) are heated by a steam coil to 60° to 70°, a fluid paste (free from lumps) prepared in the tank *A* (furnished with a stirrer) from 500 kilos of chloride of lime (35 per cent. of available chlorine) and about 1000 litres of water being then run in continuously through the funnel *a* and tube *b* to the bottom of *B*. The reaction is instantaneous, and when all the hypochlorite has been added, the temperature is maintained at 60° (*B* being jacketed) until the whole of the chloroform is distilled off and condensed in the coil *C*; the distillation is followed either by means of a hydrometer under the bell-jar *e*, through which the condensate passes, or by diluting a sample with water:

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and less dangerous, since the insensibility extends only to one organ or one region of the subject of the operation.

So that, to *chloroform, ether,* etc., was added, in 1885, *cocaine,* which paralyses only the sensitive peripheral nerves without influencing the motor nerves. By studying anæsthetic and hypnotic substances chemists were able to determine what specific atomic groups produced anæsthetic properties in a molecule. Thus, with many of these substances, it was found to be the hydroxyl group which induced sleep, especially when it is united to carbon joined at the same time to several alkyl groups; replacement of the hydroxyl by other groups resulted in the disappearance of the anæsthetic properties. Also various amino-acid groups, under certain definite conditions, give rise to anæsthetics. To enumerate all the members of the vast group of anæsthetics which chemistry has placed at the disposal of surgery would be out of place here, but the following few examples may be mentioned: *α-eucaine, β-eucaine, orthoform, alipine, holocaine,* and, on the other hand, *sulphonal* (*see later*), *trional, dormiol, hedonal, veronal* (*see later*), etc. Other properties of anæsthetics are described in Part III, in the section on Alkaloids.

no chloroform should separate. The chloroform is then drawn off through the tap *d* and the distillation continued at a temperature above 60°, the alcohol passing over being collected in *D* and then passed into *E*; this distillation is stopped when the distillate contains less than 2 per cent. of alcohol. The concentration and quantity of this dilute alcohol (about 1800 litres) are determined, the liquid being then forced through the tube *g* into *B*, which has been previously emptied through *h*. Further alcohol is then added to give the amount first used, and a second operation with 500 kilos of calcium hypochlorite carried out.

By this process 100 kilos of pure chloroform are obtained on the average from 1022 kilos of calcium hypochlorite (with 35 per cent. of available chlorine) and 77 kilos of 94 per cent. alcohol, whereas with the proportions of reagents formerly in use as much as 100 kilos of alcohol and 1300 kilos of hypochlorite were consumed.

In recent years successful use has been made of the method of making chloroform from acetone, which is now obtainable cheap and very pure (quite neutral and with less than 0·05 per cent. of aldehyde), the chloroform thus prepared being highly pure. Except for the reaction vessel, the plant is similar to that of the alcohol process. This vessel is furnished, besides with a jacket, with an efficient stirrer and, in its upper part, with a perforated or gauze disc to break the froth, since the reaction is at first rapid and, if not regulated, may become violent and dangerous. To the mixture (free from lumps) of calcium hypochlorite (250 kilos) and water (800 litres), heated to 50° in the boiler, is slowly (in about an hour) added 28 litres of acetone, the mass being cooled to prevent the temperature from exceeding 55° at first, and 60° at the end of the addition. The condensed chloroform of sp. gr. 1·5 is collected, while that finally distilling over with sp. gr. 1·45 (by heating to 85°) is set apart for the succeeding operation, as it contains a little acetone. The crude chloroform obtained is washed with a little water and sodium carbonate, then stirred with one-third of its volume of water and decanted from the latter, and afterwards washed two or three times, in a lead-lined vessel fitted with a stirrer, with a little 66° Bé. sulphuric acid until the acid is no longer turned brown. After the acid has been thoroughly removed from the chloroform, this is washed with water, dried over $CaCl_2$, and distilled from a copper still. The washing with water and the drying may be omitted, the chloroform being then distilled with a little soda to neutralise traces of acid and the first and last portions of the distillate kept separate. The bulk of the chloroform distilled is highly pure and the yield is 205 kilos of a crude product from 100 kilos of acetone and 1110 kilos of hypochlorite (about 34 per cent. of active Cl); 175 kilos of pure chloroform [1] are obtained.

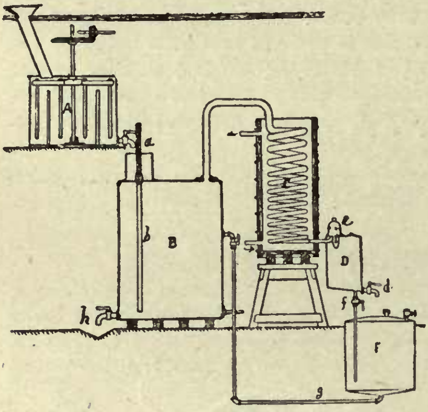

FIG. 104.

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[1] **TESTS FOR CHLOROFORM.** Minute quantities of chloroform may be detected by heating a little of the liquid gently with a few drops of aniline and of alcoholic potash solution, the characteristic repulsive odour of phenylcarbylamine (phenyl isocyanide) being formed. Pure chloroform for medicinal use should not be acid or give a precipitate with silver nitrate solution or redden potassium iodide solution; on evaporation it should not leave a residue of water or odorous substances, and it should not darken with concentrated sulphuric acid. To test for the presence in it of carbon tetrachloride, 20 c.c. are treated with a solution of 3 drops of aniline in 5 c.c. of benzene; turbidity or separation of crystals of phenylurea indicates with certainty the presence of the tetrachloride. To ascertain if it contains alcohol it is treated with a very dilute potassium permanganate solution, which is decolorised in presence of this impurity.

Its estimation is effected by treating a given weight with Fehling's solution (*see* under Sugar Analysis) and heating the mixture in a *closed* bottle on a water-bath for some hours (until the odour of chloroform disappears), the cuprous oxide, formed according to the equation, $CHCl_3 + 2CuO + 5KOH = K_2CO_3 + 3H_2O + 3KCl + Cu_2O$, being weighed. One molecule of chloroform corresponds with 2 atoms of copper.

It may be determined also by heating with alcoholic potash in a reflux apparatus on the water-bath; it is then diluted with water, the alcohol distilled off, and the potassium chloride formed (together with potassium formate, *see* preceding page) titrated with a standard silver nitrate solution. *This method serves for the estimation of all alkyl-halogen compounds.*

During recent years the industrial preparation of chloroform has again been attempted by electrolysing an aqueous solution of KCl (20 per cent.) into which alcohol or acetone is slowly introduced; if the temperature is kept at about 60°, the chloroform distils off as it is formed. In this process 1 h.p.-hour is consumed to produce 40 grams of chloroform (L. Zambelleti, 1899).

According to the Besson process (Ger. Pat. 129,237), continuous production and a good yield are obtained by heating, in a vessel divided into cells communicating below, alcohol previously chlorinated to the sp. gr. 35° Bé. with chloride of lime and alkali in the hot.

Attempts have been made to prepare chloroform industrially by reducing carbon tetrachloride in the hot with nascent hydrogen: $CCl_4 + H_2 = HCl + CHCl_3$, but the product is contaminated with CCl_4 and CS_2 (used in making the CCl_4) which are eliminated with difficulty.

Erlworthy and Lange (Fr. Pat. 354,291, 1905) propose to produce chloroform from methane and chlorine diluted with indifferent gases (N, CO_2) by subjecting the mixture to the action of light in suitable retorts: $CH_4 + 6Cl = 3HCl + CHCl_3$, but the process has apparently not been applied in practice, although in 1913 improved results were obtained with ultra-violet rays.

The pre-war price of industrial chloroform was about £8 per 100 kilos; redistilled cost 2*s.* 10*d.* per kilo; the pharmacopœial preparation 2*s.* 2*d.*; puriss. from chloral, 6*s.* 5*d.* to 9*s.* 7*d.*; Pictet's, 12*s.* per kilo, and that of Anschütz 10*d.* per 50 grams. Part of the chloroform consumed in Italy is imported from abroad, the Italian output prior to the war being about 10 tons per annum.

In 1909 Germany exported 150 tons of chloroform, while Great Britain imported 16 cwt. and exported 14 cwt. in 1910. The United States imported 8 cwt. in 1910.

IODOFORM (Tri-iodomethane), CHI_3, was discovered by Serullas in 1822, and its constitution was established by Dumas who, unlike his predecessors, did not overlook the very small proportion of hydrogen (0·25 per cent.) present.

It is formed by heating ethyl alcohol or acetone with iodine and sufficient alkali hydroxide or carbonate to decolorise the iodine (*Lieben's reaction*):

$$C_2H_5OH + 8I + 6KOH = CHI_3 + H \cdot COOK + 5KI + 5H_2O.$$

This reaction (separation of yellow crystals and formation of a characteristic odour) is so sensitive that it serves for the detection of minute traces (1 : 2000) of ethyl alcohol or acetone in other liquids (waiting twelve hours for the separation of crystals if the amount of alcohol is small); the same reaction is, however, given by isopropyl alcohol, acetaldehyde (and by almost all compounds containing the group $CH_3 \cdot CO \cdot$), but not by methyl alcohol, ether, or acetic acid.

For the practical preparation of iodoform 32 parts of K_2CO_3 are dissolved in 80 parts of water and 16 parts of alcohol, the mixture being heated to 70° and 32 parts of iodine gradually added. The separated iodoform is filtered off and the iodine of the potassium iodide in the filtrate utilised as follows: 20 parts of HCl are added and 2 to 3 parts of potassium dichromate, the liquid being then neutralised with K_2CO_3, mixed with a further 32 parts of K_2CO_3, 16 parts of alcohol and 6 parts of iodine. On heating, a second quantity of iodoform separates, and after this or another similar operation the mother-liquor is treated to recover the iodine from the potassium iodide.

It has been proposed to prepare iodoform by treating the metallic acetylides (*see* p. 110) with iodine and caustic soda.

It seems that practical use is now made of the electrolytic process, using a bath of 6 parts KI, 2 parts soda, 8 vols. alcohol, and 40 of water at 60° to 65°. The iodine to be used in the reaction is set free at the anode, and to avoid the formation of a little iodate with the KOH formed at the cathode the latter is enclosed in parchment paper.

When pure, iodoform crystallises in hexagonal, yellow plates (sp. gr. 2), insoluble in water but soluble in alcohol or ether. It has a penetrating and persistent odour, recalling partly that of saffron and partly that of phenol. It melts at 119°, readily sublimes, and is volatile in steam. When heated with either alcohol or reducing agents, it gives methylene iodide.

It is used in surgery as an important antiseptic, which, however, acts indirectly on bacteria by means of the decomposition products formed from it under the action of the pus of wounds or of the heat of the body.

TESTS FOR IODOFORM. It should leave no residue on sublimation and should dissolve completely in alcohol or ether. It is estimated by heating about 1 gram with about 2 grams of silver nitrate and 25 c.c. of concentrated nitric acid (free from chlorine) in a reflux apparatus so that the liquid does not boil; when the nitrous vapours have disappeared the liquid is diluted with water to 150 c.c. and heated, the silver iodide being collected on a tared filter, dried and weighed: 1·789 grams AgI corresponds with 1 gram iodoform.

Owing to its disagreeable odour, it has been to some extent replaced latterly by **Xeroform**, which is a *tribromophenoxide of bismuth*, $C_6H_2Br_3O \cdot OH, Bi_2O_2$, obtained by the action of bismuth chloride on sodium tribromophenoxide, and forming a tasteless, odourless, yellow powder insoluble in water or alcohol; it is used also as a disinfectant for the intestines, and costs 44*s.* to 48*s.* per kilo, whilst iodoform costs only 24*s.* to 28*s.* a kilo.

CARBON TETRACHLORIDE (Tetrachloromethane), CCl_4 (*see* Vol. I., p. 470).

POLYCHLORO-DERIVATIVES OF ETHYLENE AND ETHANE.[1] Asymm.

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[1] Since 1908 (Ger. Pats. 196,324, 204,516, 204,883, etc.), the Chemische Fabrik Griesheim-Elektron of Frankfort, and the Usines électriques de la Lonza of Geneva have placed on the market, as *non-inflammable solvents* for industrial purposes, six chlorinated compounds obtained as colourless liquids by the action of chlorine on acetylene. They are all good solvents for fats, resins, rubber, bitumen, sulphur, etc., and can replace advantageously benzine, carbon disulphide, and alcohol, since they are not inflammable and their vapours do not form explosive mixtures with air; over carbon tetrachloride they have the advantage of not attacking the metal parts of the extraction apparatus, and the loss on extraction varies from 0·3 to 0·8 per cent.; they are, however, dearer than the ordinary solvents and seem to be injurious to health. *Acetylene tetrachloride* (*tetrachloroethane*) was prepared in 1903 by the Consortium für elektrochemische Industrie of Nuremberg (Ger. Pat. 154,657) by the interaction of acetylene and chlorine in presence of antimony chloride as catalyst. *Dichloroethylene*, used in the manufacture of thio-indigo, is formed quantitatively from tetrachloroethane by the action of ordinary metals in the hot in presence of a little water (Ger. Pat. 217,554). *Trichloroethylene* is obtained from tetrachloroethane by heating it with lime (Ger. Pat. 170,900); by treatment of the products gradually forming with lime and chlorine alternately, C_2HCl_5, C_2Cl_4 and C_2Cl_6 (solid) may be prepared.

With trichloroethylene various organic syntheses may be effected. Thus, with sodium ethoxide it yields *dichlorovinyl ether*, $C_2HCl_2 \cdot OC_2H_5$; this, in its turn, exhibits marked reactivity, and on addition of Cl or HCl gives saturated products which, on distillation, liberate ethyl chloride and form *mono-* and *di-chloroacetyl chlorides*, $C_2H_2Cl_2O$ and C_2HCl_3O. With water in presence of a trace of HCl (as catalyst) at the ordinary temperature, dichlorovinyl ether gives quantitatively *ethyl chloroacetate*, $CH_2Cl \cdot COOC_2H_5$ (Ger. Pats. 210,502 and 216,716), which was first obtained from acetic acid and is now more economically derived from acetylene; it is used in numerous important syntheses, including that of indigo.

The properties of these compounds are given in the following Table:

	DICHLORO-ETHYLENE	TRICHLORO-ETHYLENE	TETRA-CHLORO-ETHYLENE	TETRA-CHLORO-ETHANE	PENTA-CHLORO-ETHANE	HEXA-CHLORO-ETHANE
	$C_2H_2Cl_2$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
Common name . .	*Dieline*	*Trieline*	*Etiline*	*Tetraline*	*Pentaline*	—
Specific gravity . .	1·278 (1·25)	1·471	1·628	1·600	1·685 (1·70)	2
Boiling-point . .	52° (55)	85° (88)	119° (121)	144° (147)	159°	(185°)
Vapour pressure at 20°	205 mm.	56	17	11	7	3
Specific heat at 20° .	0·270	0·223	0·216	0·268	0·266	—
Heat of evaporation .	41 cals.	57·8	50	52·8	45	—
Freezing-point . .	—	− 73°	− 19°	− 36°	− 22°	—
Uses and properties .	Readily dissolves rubber	Dissolves fats, paraffin wax and vaseline better than benzine	Serves well for removing spots	Dissolves resins and varnishes, like turpentine and alcohol and dissolves cellulose acetate for films and artificial silk	Readily dissolves cellulose acetate for artificial silk and cinematograph films	Has an odour like camphor, and serves as an insecticide
Ger. Pats. 201,705 204,516 216,070 254,068		Ger. Pats. 171,900 206,854				

Trichloroethylene, C_2HCl_3, is used also as a non-inflammable solvent in chemical cleaning works, in the manufacture of oils and fats, in making lacs, and in one of the syntheses of indigo: with sodium ethoxide it gives *dichlorovinyl ether*, which with water yields ethyl chloroacetate,

HEPTACHLOROPROPANE was prepared in 1910 by Böeseken and Prins from tetrachloroethylene and chloroform in presence of aluminium chloride as catalyst.

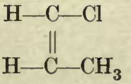
II. HALOGENATED DERIVATIVES OF UNSATURATED HYDROCARBONS

These are obtained from saturated halogen derivatives by partial elimination of the halogen hydracid: $C_2H_4Br_2 = HBr + C_2H_3Br$. They are formed also by incomplete saturation, with halogens or halogen hydracids, of the less saturated hydrocarbons: $C_2H_2 + HBr = C_2H_3Br$ (*see* Table in footnote).

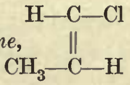
Bromoacetylene, $CH \vdots CBr$, is a gas liquefying at — 2° and ignites spontaneously in the air. It gives brilliant luminescent effects, even if mixed with air. It ozonises atmospheric oxygen, but the latter is not ionised, as is the case with phosphorus.

The allyl compounds, C_3H_5X, are formed from allyl alcohol by the action either of halogen hydracid or of phosphorus and halogen.

ALLYL CHLORIDE (Chloro-3-propene-1), $CH_2 : CH \cdot CH_2Cl$; the *bromide* and *iodide* have analogous constitutions. These are related to the natural allyl compounds (garlic oil and mustard oil). Two stereoisomerides are known:

a-chloropropylene, 

$$\begin{array}{c} H—C—Cl \\ \| \\ H—C—CH_3 \end{array}$$

and *iso-a-chloropropylene*, 

$$\begin{array}{c} H—C—Cl \\ \| \\ CH_3—C—H \end{array}$$

TETRABROMOETHANE, $CHBr_2 \cdot CHBr_2$ (improperly termed *acetylene bromide*) is prepared industrially in the impure state by passing bromine in at the top of a cooled earthenware coil and acetylene in at the bottom, the liquid product collecting at the bottom: $C_2H_2 + 2Br_2 = C_2H_2Br_4 + 64$ cals. It boils at 215° with partial decomposition and does not solidify at — 20°. It contains 92·5 per cent. of bromine and has a high specific gravity (2·943), and on this account is used for the mechanical separation of mineral components; thus large quantities are employed to separate diamonds (sp. gr. 3·35) from the sands of Western Africa (sp. gr. 2·4). It is despatched in vessels similar to those used for bromine. It is obtained pure by treatment with alcohol and zinc dust, which converts it into dibromoacetylene; the latter is then purified by distillation and transformed into the tetrabromo-compound by means of bromine.

CC. ALCOHOLS

These form an important group of organic compounds containing one or more characteristic hydroxyls, the hydrogen of which has pronounced reactive properties, so that numerous series of other compounds are derived from the alcohols. They have a neutral reaction, although their chemical behaviour is analogous to that of the inorganic bases which always contain the anion OH′. The majority of these alcohols are colourless liquids, but those of high molecular weights are oily, solid, and sometimes yellowish. The first members of the series are soluble in water, but with increase of molecular weight the solubility decreases and the smell, generally slight, also tends to disappear. They are often found in nature either free or combined with organic acids, in the fats, waxes, fruits, essential oils, etc.

According to the number of hydroxyl groups they contain, they are divided into *mono-*, *di-*, . . . *polyhydric alcohols*, and may belong either to the saturated or to the unsaturated series—already studied in connection with the hydrocarbons—of which they retain the fundamental characters; added to the latter are those characteristic of the alcoholic group, which we shall study generally with the monohydric alcohols.

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and this, with aniline in presence of calcium carbonate, forms the ethyl ester of phenylglycine; with potassium carbonate the latter gives the corresponding potassium salt, which gives rise to indigo on condensation with calcium silicide (*see* Vol. I., p. 500).

The existence of cis- and trans-stereoisomerides of symmetrical *dichloroethylene*, CHCl : CHCl, appears proved.

I. SATURATED MONOHYDRIC ALCOHOLS

The specific gravity of these is always lower than that of water, and up to the C_{16} member they distil unchanged at the ordinary pressure; beyond that reduced pressure must be employed.

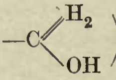
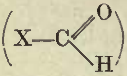
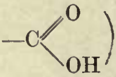
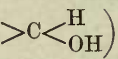
That alcohols always contain a hydroxyl group, OH, may be shown by the following chemical reactions:

The alcohols may be obtained by the action of silver hydroxide, $Ag \cdot OH$ (which certainly contains the group OH), or even of the alkalis or hot water, on halogenated hydrocarbons: $C_nH_{2n+1}I + AgOH = AgI + C_nH_{2+n1}OH$.

With the halogen hydracids the hydroxyl separates from the alcohols in the form of water: $C_nH_{2n+1}OH + HBr = H_2O + C_nH_{2n+1}Br$; the same happens with oxyacids, the so-called *esters* being formed: $C_nH_{2n+1}OH + HNO_3 = H_2O + C_nH_{2n+1}NO_3$. Just as sodium and potassium react with water, liberating hydrogen, so do they act on the alcohols, from which only the *typical hydrogen* (hydroxylic), not united directly to carbon, is eliminated: $C_nH_{2n+1}OH + Na = C_nH_{2n+1}ONa$ (*sodium alkoxide*) + H. *Magnesium alkoxides* are also easily obtained. With phosphorus trichloride, however, the hydroxyl group is eliminated:

$$3C_nH_{2n+1}OH + PCl_3 = 3C_nH_{2n+1}Cl + P(OH)_3.$$

On p. 17 the difference in constitution between ethyl alcohol and methyl ether has been demonstrated.

If the hydroxyl group occurs in place of a hydrogen atom in the *methyl* group ($—CH_3$) at the extremity of the hydrocarbon chain, the *primary alcohols* are obtained, all containing the characteristic group $—CH_2 \cdot OH$ (*i. e.*,  $—C\langle^{H_2}_{OH}$), *e. g.*, propyl alcohol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$, and by oxidation of these alcohols are formed first *aldehydes* with the characteristic group ( $X—C\langle^{O}_{H}$), and then *acids* with the characteristic *carboxyl* group $—COOH$ (*i. e.*,  $—C\langle^{O}_{OH}$). Substitution of a hydroxyl for a hydrogen atom in an intermediate *methylene* group ($= CH_2$) in the saturated hydrocarbon chain yields *secondary alcohols*, which have the characteristic group $>CH \cdot OH$ (*i. e.*,  $>C<^{H}_{OH}$) and on oxidation give *ketones* containing the special group $>CO$. Finally the substitution of the hydrogen of a branched hydrocarbon may take place in the *methinic* group ($\equiv CH$), giving *tertiary alcohols* with the characteristic grouping $\equiv C \cdot OH$, the other three valencies of the carbon being united to three carbon atoms. When the secondary alcohols are oxidised they cannot give either acids or ketones with an equal number of carbon atoms, but, if the oxidation is energetic, the chain breaks, and then acids and ketones may be formed, but with less numbers of carbon atoms.

According to B. Neave (1909), primary, secondary, and tertiary alcohols may be distinguished by the *Sabatier and Senderens reaction* (*see* p. 35), by passing the vapour of the alcohol over finely divided copper heated at 300°: the primary alcohols form hydrogen and aldehydes (recognisable by Schiff's reaction; *see* section on Aldehydes), the secondary ones give hydrogen and ketones (detectable by semicarbazide hydrochloride solution) and the tertiary alcohols give water and unsaturated hydrocarbons (which decolorise bromine water).

The primary alcohols and the corresponding ethers have the highest boiling-points, the tertiary ones and, in general, those with branched chains showing the lowest boiling-points.

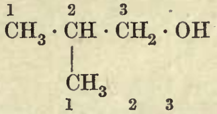
In the group of alcohols the *isomerism* and the number of isomerides are similar to those of the halogenated derivatives of the hydrocarbons, since the halogen atom is here replaced by a hydroxyl group.

The *names* of the primary alcohols are made from those of the corresponding hydrocarbons (*see* p. 30), with the termination *ol*, and those of the secondary and tertiary alcohols are derived from the names of the hydrocarbons with the longest non-branched chains; or the secondary and tertiary alcohols may be regarded as derivatives of methyl alcohol or *carbinol*, $CH_3 \cdot OH$, formed by substitution of the hydrogen atoms of the methyl group. We have, hence, two different, but still equally clear, systems of nomenclature. For example:

(1) *Normal butyl alcohol:* $CH_3 \cdot CH_2 \cdot \underset{2}{CH_2} \cdot \underset{1}{CH_2} \cdot OH$ = butan-1-ol or n-propylcarbinol.

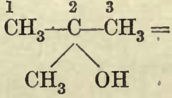
(2) *Secondary butyl alcohol:* $CH_3 \cdot CH_2 \cdot \underset{2}{CH(OH)} \cdot \underset{1}{CH_3}$ = butan-2-ol or methylethylcarbinol.

(3) *Isobutyl alcohol:*



$\overset{1}{CH_3} \cdot \underset{\underset{CH_3}{|}}{\overset{2}{CH}} \cdot \overset{3}{CH_2} \cdot OH$ = 2-methylpropan-3-ol or isopropylcarbinol.

(4) *Tertiary butyl alcohol:*

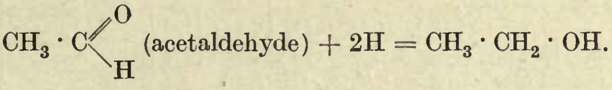


$\overset{1}{CH_3}\text{—}\underset{CH_3 \quad OH}{\overset{2}{C}}\text{—}\overset{3}{CH_3}$ = 2-methylpropan-2-ol or trimethylcarbinol.

PROCESSES OF FORMATION OF MONOHYDRIC ALCOHOLS. As well as from the halogen derivatives, the alcohols may usually be obtained by decomposing esters with acids, alkalis, or superheated water. This reaction is termed *saponification* or *hydrolysis*:

$$C_2H_5O \cdot NO_2 + KOH = KNO_3 + C_2H_5 \cdot OH.$$

In a general way, the *primary alcohols* are formed by reducing the acids ($C_nH_{2n}O_2$) or aldehydes ($C_nH_{2n}O$) with nascent hydrogen:



$$CH_3 \cdot C\begin{matrix}\nearrow O \\ \searrow H\end{matrix} \text{ (acetaldehyde)} + 2H = CH_3 \cdot CH_2 \cdot OH.$$

Since the acids, in their turn, may be prepared from the alcohols with one carbon atom less, we have at our disposal a general reaction for preparing synthetically any higher alcohol.

The *secondary alcohols* are formed by reducing the ketones, $C_nH_{2n}O$, *e. g.*:

$$\underset{\text{Acetone}}{CH_3 \cdot CO \cdot CH_3} + H_2 = \underset{\text{Isopropyl alcohol}}{CH_3 \cdot CH(OH) \cdot CH_3}$$

(*see later*, Aldehydes and Ketones).

The *tertiary* alcohols are formed by the *prolonged* action of zinc methyl on acid chlorides, the intermediate compounds thus formed being decomposed with water.

For the *secondary* and *tertiary* alcohols Grignard's reaction may also be employed (*see later*, Alkylmetallic Compounds).

Of more industrial importance, however, is the preparation of some of the more common of these alcohols by the distillation of wood or the fermentation of certain carbohydrates (*see later*).

In addition to the properties of the alcohols given above, namely, their behaviour towards acids, halogens (which oxidise them), chlorides, and oxidising agents in general (which give aldehydes and acids), it may be mentioned that the higher alcohols (primary) are transformed into the corresponding acids by simple heating with soda lime. Traces of primary alcohols are detectable by oxidising with permanganate and sulphuric acid and then testing for aldehyde, which reddens a sulphurous acid solution of fuchsine.

PHYSICAL CONSTANTS OF THE MONOHYDRIC ALCOHOLS

	Name and Formula	Specific gravity	Melting-point	Boiling-Point
1.	Methyl alcohol, $CH_3{\cdot}OH$	0·812 (0°)	−94°, −98°	66°
2.	Ethyl alcohol, $C_2H_5{\cdot}OH$	0·806	−112°, −117°	78°
3*a*.	Normal propyl alcohol (prim.) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	0·817	−127°	97°
3*b*.	Isopropyl alcohol (sec.) $CH_3{\cdot}CH(OH){\cdot}CH_3$	0·789 (20°)	—	81°
4*a*.	Normal butyl alcohol (prim.), $C_4H_9{\cdot}OH$	0·810	−80°(−122°)	117°
4*b*.	Normal butyl alcohol (sec.), $C_4H_9{\cdot}OH$	0·808	—	100°
4*c*.	Isobutyl alcohol, $C_4H_9{\cdot}OH$	0·806 (20°)	—	107°
4*d*.	Tertiary butyl alcohol (trimethylcarbinol) $C_4H_9{\cdot}OH$	0·786 (20°)	+25°	83°
5*a*.	Normal amyl alcohol (prim.) $CH_3{\cdot}[CH_2]_3{\cdot}CH_2{\cdot}OH$	0·817 (20°)	—	138°
5*b*.	Amyl alcohol of fermentation or isobutylcarbinol, $(CH_3)_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	0·810 (20°)	—	130°
5*c*.	Active amyl alcohol or sec. butylcarbinol, $CH_3{\cdot}CH(C_2H_5){\cdot}CH_2{\cdot}OH$	0·816 (20°)	—	128°
5*d*.	Trimethyl- or tertiary butyl-carbinol, $(CH_3)_3C{\cdot}CH_2{\cdot}OH$	0·812 (20°)	49°	113°
5*e*.	Diethylcarbinol, $C_2H_5{\cdot}CH(OH){\cdot}C_2H_5$	0·831 (0°)	—	117°
5*f*.	Methylpropylcarbinol, $CH_3{\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CH_3$	0·824 (0°)	—	119°
5*g*.	Methylisopropylcarbinol, $(CH_3)_2CH{\cdot}CH(OH){\cdot}CH_3$	0·819 (0°)	—	112·5°
5*h*.	Dimethylethylcarbinol, $(CH_3)_2C(OH){\cdot}C_2H_5$	0·814 (15°)	−12°	102°
6.	Normal hexyl alcohol (prim.), $C_6H_{13}{\cdot}OH$	0·833 (0°)	—	157°
7.	Normal heptyl alcohol (prim.), $C_7H_{15}{\cdot}OH$	0·836	—	175°
8.	Normal octyl alcohol (prim.), $C_8H_{17}{\cdot}OH$	0·839	—	191°
9.	Normal nonyl alcohol, $C_9H_{19}{\cdot}OH$	0·842	−5°	213°
10.	Decyl alcohol, $C_{10}H_{21}{\cdot}OH$	0·839	+7°	231°
11.	Undecyl alcohol, $C_{11}H_{23}{\cdot}OH$	—	+19°	131° (15mm.)
12.	Dodecyl alcohol, $C_{12}H_{25}{\cdot}OH$	0·831	24°	143° „
13.	Tridecyl alcohol, $C_{13}H_{27}{\cdot}OH$	—	30·5°	156° „
14.	Tetradecyl alcohol, $C_{14}H_{29}{\cdot}OH$	0·824	38°	167° „
15.	Pentadecyl alcohol, $C_{15}H_{31}{\cdot}OH$	—	45–46°	—
16.	Hexadecyl (cetyl) alcohol, $C_{16}H_{33}{\cdot}OH$	0·818	50°	190° „
17.	Octodecyl alcohol, $C_{18}H_{37}{\cdot}OH$	0·813	59°	211° „
18.	Ceryl alcohol, $C_{26}H_{53}{\cdot}OH$	—	79°	—
19.	Myricyl alcohol, $C_{30}H_{61}{\cdot}OH$	—	85°	—

By the behaviour of the nitro-compounds (prepared from the corresponding iodides and silver nitrite) and also by the initial velocity and degree of esterification, primary alcohols may be differentiated from the secondary and tertiary ones.

Various primary normal alcohols enter inorganic compounds as *alcohol of crystallisation*, *e. g.*, $BaO, 2CH_3 \cdot OH$; $CaCl_2, 4CH_3 \cdot OH$; $KOH, 2C_2H_5 \cdot OH$; $MgCl_2, 6C_2H_5 \cdot OH$; $CaCl_2, 4C_2H_5 \cdot OH$, etc.; it is hence evident why calcium chloride cannot be used for drying alcohol, although it serves well in the case of ether.

METHYL ALCOHOL, $CH_3 . OH$ (Methanol or Carbinol)

This is also called *wood-spirit*, since it was obtained by Boyle in 1661 from wood-tar, and is to-day prepared in large quantities by distilling wood. Its chemical composition was not determined until 1834 (by Dumas and Peligot).

In nature it occurs in the form of its salicylic ester, in *Gaultheria procumbens* (in Canada) and as butyric ester in the bitter seeds of *Heracleum giganteum*.

PROPERTIES. When pure it is a colourless liquid, b.-pt. 66°, with a faint alcoholic smell; it burns with a non-luminous flame, solidifies at very low temperatures, and melts at − 94°. When 1 kilo is burned, 5310 cals. are developed, and its heat of evaporation is 262·2 cals. Its vapour pressure at different temperatures is as follows (mm. of mercury).

Temperature .	− 10°	0°	20°	30°	40°	50°	60°	80°	100°
Pressure . .	15·5	29·6	96	160	260	406	625	1341	2621

It dissolves in all proportions in water, alcohol, ether, or chloroform. Its specific gravity at 15° is 0·7984 (at 64·8°, 0·7476), and in aqueous solution the amount of the alcohol present may be determined from the specific gravity.[1]

Like spirits of wine (ethyl alcohol) it is intoxicating, dissolves fats, oils, etc., and even when anhydrous it dissolves calcined copper sulphate, forming a bluish-green solution.

Methyl alcohol is less poisonous than higher alcohols, but in the animal, especially in the human organism, it undergoes transformations which render it far more injurious than ethyl alcohol. The latter is subjected to rapid combustion in the organism, whereas methyl alcohol is slowly oxidised with formation of formic acid, this behaving quite differently from all other organic acids owing to its aldehydic character.

The process of oxidation of methyl alcohol varies in organisms of different species, and perhaps in different individuals of the same species, and since methyl alcohol is absorbed especially by definite nerve elements, it is in these that the slow oxidation occurs, causing serious disturbances and consequences

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[1]

Specific gravity at 15·56°	Per cent. by weight of the alcohol	Specific gravity at 15·56°	Per cent. by weight of the alcohol	Specific gravity at 15·56°	Per cent. by weight of the alcohol	Specific gravity at 15·56	Per cent. by weight of the alcohol	Specific gravity at 15·56°	Per cent. by weight of the alcohol
0·99729	1	0·96524	22	0·93335	42	0·89358	62	0·84521	82
0·99554	2	0·96238	24	0·92975	44	0·88905	64	0·84001	84
0·99214	4	0·95949	26	0·92610	46	0·88443	66	0·83473	86
0·98893	6	0·95655	28	0·92237	48	0·87970	68	0·82938	88
0·98569	8	0·95355	30	0·91855	50	0·87487	70	0·82396	90
0·98262	10	0·95053	32	0·91465	52	0·87021	72	0·81849	92
0·97962	12	0·94732	34	0·91066	54	0·86535	74	0·81293	94
0·97668	14	0·94399	36	0·90657	56	0·86042	76	0·80731	96
0·97379	16	0·94055	38	0·90239	58	0·85542	78	0·80164	98
0·97039	18	0·93697	40	0·89798	60	0·85035	80	0·79589	100
0·96808	20								

With methyl alcohol solutions of different concentrations there correspond, on boiling, vapours richer in alcohol:

Per cent. of alcohol in solution	5	10	15	20	25	30	40	50	60	70	80	90	95
Per cent. of alcohol in vapour	28	47	57	64	69	72	78	82	86	89·6	93	96·5	98·3

harmful to the human organism; fatty degeneration of the liver is also produced (E. Harnack, 1912).[1]

When heated with soda lime or with oxidising agents it readily yields formaldehyde and formic acid, and sometimes carbon dioxide; when distilled with zinc dust it gives CO and H. With potassium it forms a crystalline alcoholate, $CH_3 \cdot OK$, $CH_3 \cdot OH$, while with sodium it gives $CH_3 \cdot ONa$, $2CH_3 \cdot OH$, which loses the alcohol at 170°.

With alkalies and with salts it forms additive products, *e. g.*, $5NaOH + 6CH_3 \cdot OH$ and $CaCl_2 + 4CH_3 \cdot OH$.

Laboratory Preparation. Very pure methyl alcohol may be prepared by dissolving 100 grams of iodine in 1 kilo of commercial 80 to 85 per cent. methyl alcohol, adding sufficient caustic soda solution to decolorise the liquid, and slowly distilling or rectifying.

INDUSTRIAL PREPARATION. Methyl alcohol is obtained industrially by the dry distillation of wood, it being a bye-product in the manufacture of acetic acid (*q. v.*). The liquid products of the distillation contain much water, about 6 to 8 per cent. of acetic acid, 1 to 1·5 per cent. of methyl alcohol, 0·1 to 0·4 per cent. of acetone, and a certain amount of tar. After the removal of the tar, the liquid is neutralised with lime and distilled, this yielding dilute (about 10 per cent.) methyl alcohol solution contaminated with various products, especially acetone, tar, etc. The liquid is next distilled with about 2 per cent. of lime) in a rectifying apparatus (*see later:* Ethyl alcohol). The resultant product constitutes *crude methyl alcohol* (*wood spirit*), which is almost colourless at first, but becomes brownish-red in the air; its specific gravity is about 0·816, and it contains about 80 per cent. of methyl alcohol, 10 to 14 per cent. of acetone, and small proportions of other impurities (acetaldehyde, formaldehyde, allyl alcohol, furfural, methyl ethyl ketone, dimethylacetal, methyl acetate, catechol, ammonia, pyridine, methylamine, etc.).

To *purify* it, it is diluted with water to the sp. gr. 0·935 (about 40 per cent.), left for several days, and after the superficial tarry layer which collects has been removed it is treated with 2 per cent. of lime and distilled almost completely. The distilled product is mixed with 0·1 to 0·2 per cent. of sulphuric acid and rectified, the foreshots (rich in acetone and allyl alcohol) and tailings (rich in wood-oil and high boiling-point ketones of almost no practical value), being collected separately. The large fraction (about 50 per cent.) which distils over slowly at 62° to 65° serves in most countries for denaturing ethyl alcohol and for making formaldehyde, and another portion (about 25 per cent.) which is distilled still more carefully at 65° to 66° constitutes the *pure methyl alcohol* used for synthetic organic products. The last traces of acetone are removed by distillation in presence of a little calcium hypochlorite, which forms chloroform with the acetone (also with methyl alcohol). Better purification is effected by transforming the alcohol into an ester (*e. g.*, the oxalate, by treatment with concentrated sulphuric acid and potassium dioxalate), which is easily separated from the impurities; by hydrolysing the ester with KOH, distilling and rectifying, pure methyl alcohol is obtained. The acetone may also be got rid of by combining the alcohol with $CaCl_2$, giving the compound $CaCl_2, 4CH_3 \cdot OH$, which is stable at 100°, so that the acetone may be distilled off at 56° together with the other impurities; the residue is then decomposed with water and the pure methyl alcohol distilled. The empyreumatic odour may be removed by filtration through wood charcoal.

According to Farkas's patent (Ger. Pat. 166,360, 1904) alcohol of 92 to 95 per cent. purity is obtained direct if the vapours from the distillation of wood, while still hot, are

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[1] In Berlin at the end of 1911 some dozens of people died suddenly and some hundreds incurred serious danger from drinking spirits consisting to the extent of four-fifths of methyl alcohol. The trial, investigations and reports which followed in 1912 (Scharmach case) showed that even before then there were numerous cases of poisoning of workmen due to respiration of vapours of methyl alcohol during the manufacture, or to ingestion of spirits adulterated with this alcohol. As little as 8 grams suffices to cause serious effects on the eyesight, and larger doses lead to blindness. Nearly three hundred cases of such poisoning were registered in the literature up to 1904. Direct post-mortem detection of methyl alcohol is difficult, but abnormal quantities of formic acid appear in the bladder, brain, stomach, etc. In 1911 abnormally large quantities of methyl alcohol were imported into Italy, these being probably added as adulterant to ethyl alcohol; this abuse was met by the imposition of taxation equal to that on ethyl alcohol, namely, £10 16*s.* per anhydrous hectolitre.

passed through hot NaOH solution (15° to 20° Bé.), which fixes the acid products, and then into hot fatty acids, which fix the methyl alcohol; the alcohol recovered from these fatty acids is purified by passing the vapours into milk of lime and then rectifying.

To ascertain if the alcohol still contains acetone, 10 c.c. of it is treated with caustic soda and an aqueous solution of iodine in potassium iodide; no turbidity due to iodoform should be formed for some time.[1]

USES AND STATISTICS. Methyl alcohol is used mainly for the manufacture of formaldehyde and of methyl derivatives (dimethylaniline, methyl chloride and bromide, etc.) used in making aniline dyes. It is employed also in the preparation of different varnishes as a substitute (partial or total) for spirit and oil of turpentine, in preparing perfumed hair lotions, etc., and for denaturing spirit (ethyl alcohol).

In 1902, Germany produced 5000 tons of the pure alcohol, of which 1151 tons were exported, and imported 4273 tons of the crude product. In 1909 7000 tons of the crude alcohol were imported and in 1910, 9000 tons, one-half from Austria and one-half from North America at £24 per ton in 1909 and £30 in 1910. In the latter year 2000 tons of pure methyl alcohol were exported at £40 per ton.

The Italian importation and exportation were as follows (hectolitres):

	1908	1910	1911	1913	1914	1915	1916	1917
Importation . . .	25	640	2916	296	1611	275	—	2
Exportation . . .	662	17	5	11	11	10	32	—

For France the quantities are (tons):

	1913	1914	1915	1916
Importation . . .	2269	1307	1767·5	1702
Exportation . . .	139·5	48·6	95·7	31

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[1] **Tests for Methyl Alcohol.** When *pure* it should leave no residue on evaporation, should not have an acid reaction towards litmus, and should not contain ethyl alcohol, which may be detected as follows: a little of the liquid is heated with sulphuric acid, diluted with water and distilled, the distillate being treated with permanganate, then with sulphuric acid, and finally with sodium hydrogen sulphite; if ethyl alcohol is not present this liquid will not give a violet coloration with fuchsine solution. Acetone and ethyl alcohol may also be detected by the iodoform reaction (*Lieben's reaction: see below and also* p. 121). Proportions of 2 to 3 per cent. of methyl alcohol may be detected by *Scudder and Riggs's reaction* (1906), which consists in treating 10 c.c. of the liquid at 25° with 5 c.c. of concentrated sulphuric acid and 5 c.c. of saturated permanganate solution, decolorising (after two minutes) with sulphurous acid solution and boiling until all smell of sulphur dioxide or acetaldehyde disappears. This liquid is then tested for formaldehyde by adding a few centigrams of resorcinol to 2 c.c. and pouring 1 c.c. of pure concentrated sulphuric acid to the bottom of the liquid; a blue ring, due to the formaldehyde formed from the methyl alcohol, forms at the surface of separation of the two liquids. Denigès (1910) detects as little as 1 per cent. of ethyl alcohol by heating the methyl alcohol with bromine water and testing for the acetaldehyde formed with fuchsine solution decolorised with SO_2 (*see* Aldehydes).

Estimation of the methyl alcohol in the commercial product is effected by the Krell-Krämer method: 30 grams of phosphorus tri-iodide is placed in a flask furnished with a long reflux condenser, down which is poured, drop by drop, 10 c.c. of the methyl alcohol; after a short time the methyl iodide formed is distilled from a water-bath into a graduated cylinder containing a little water; when the distillation is completed, the condenser is rinsed out with water and the volume of the methyl iodide under the water measured at 15°; 5 c.c. of pure methyl alcohol gives 7·19 c.c. of methyl iodide.

The *acetone* is estimated by Krämer's method: in a 50 c.c. graduated cylinder with a ground stopper are placed 10 c.c. of a 2N-caustic soda solution, then 1 c.c. of the alcohol, and, after shaking, 5 c.c. of a 2N-iodine solution. After a short time 10 c.c. of ether free from alcohol is added, the liquid shaken and then allowed to stand; the volume occupied by the ether is read off, an aliquot part of it evaporated to dryness on a tared watch-glass and the iodoform crystals dried in a desiccator and weighed: 394 parts CHI_3 correspond with 58 of acetone.

A good commercial methyl alcohol should contain not more than 0·7 per cent. of acetone and at least 95 per cent. of the alcohol; it should distil within 1°; 5 c.c. of 0·1 per cent. permanganate solution should not be decolorised immediately when treated with 5 c.c. of the alcohol, and 25 c.c. of the alcohol, mixed with 1 c.c. of an acetic acid solution of bromine (1 part Br in 80 parts of 50 per cent. acetic acid) should give a yellow solution.

In 1909 Great Britain imported 22,600 hectolitres, and in 1910 20,200 (47,200); in 1910 the value of the exports was £20,000.

The United States exported 35,000 hectolitres in 1906, 76,100 in 1910, and 92,000 (£180,000, *i. e.*, about £2 per hectolitre for the crude, about 80 per cent. alcohol); in 1914 the output of crude methyl alcohol was about 500,000 hectolitres.

Pyroligneous alcohol of 90 per cent. strength (French) was sold before the war at £4 12*s.* per 100 kilos; that of 92 to 93 per cent. strength (English) at £4 17*s.* 6*d.*; and that of 95 to 96 per cent. strength for lacs at £5 1*s.* 6*d.*; the purest methyl alcohol, free from acetone, cost £7 per 100 kilos. During the European War, the price in Italy rose to £48 per 100 kilos.

ETHYL ALCOHOL, $C_2H_5 \cdot OH$ (Ethanol, Spirit of Wine)

This is found occasionally in nature (as butyric ester in *Pastinaca sativa* and *Heracleum giganteum*) and sometimes as an abnormal product in certain vegetables and animals, whilst it is easily formed by the alteration (fermentation) of various organic vegetable substances (saccharine juices, fruits, etc.). It has hence been known from the most remote times. Aqua vitæ or spirit of wine, obtained by distilling alcoholic beverages, was used as early as the eighth century, and gave rise to an industry which acquired great renown in the province of Modena in the fourteenth century. Various European races learnt the use of aqua vitæ from the custom introduced everywhere by the soldiers, who consumed large quantities of it during the wars of the Middle Ages. Very soon, however, the northern peoples, who did not produce aqua vitæ from wine, began to prepare alcohol by suitable transformations of the starch in the cereals abounding in their countries. By the beginning of the nineteenth century alcoholic liquors (exciting and enfeebling the nervous system and the brain) were spread over the whole of the civilised world and produced the terrible social scourge of *alcoholism*, much more disastrous in its material and moral consequences than all the other maladies that afflict humanity (*see later*, Alcoholism). Later, however, alcohol gradually acquired agricultural and industrial importance owing to its increasing practical applications in the arts and industries. Since 1830 Germany has extended the manufacture of potato spirit, and in many districts great agricultural advantages have followed the cultivation of this vegetable, since the waste products from the distilleries serve as nourishment for large numbers of cattle—a source of great direct and indirect profit owing to the abundant supply of stable manure, which increases the fertility of the land and hence also the crops.

PROPERTIES. When pure, it is a colourless liquid with a characteristic odour, sp. gr. 0·7937 at 15°, 0·80625 at 0°; it boils at 78·3° (or at 13° under 21 mm. pressure), and its vapour is stable at 300°; its vapour pressures (mm. of mercury) at different temperatures are as follows:

Temperature . .	− 10°	0°	20°	30°	40°	50°	60°	70°	80°	100°
Pressure . .	6·5	12·24	44	78	133·4	219·8	350	541	812	1692

Its heat of evaporation is 216·5 cals.

At a very low temperature it gives a glassy mass, which at − 135° is converted into another solid mass m.-pt. − 117° (*enantiotropy*, Vol. I., p. 208).

When concentrated (absolute) it is extremely hygroscopic, and it mixes with water or ether in all proportions. To obtain *absolute alcohol*, *i. e.*, absolutely free from water, fractional distillation is not sufficient, since at 78·15° an aqueous alcohol containing 95·57 per cent. of alcohol by weight distils; [1]

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[1] In the following table, *a* is the percentage of alcohol by volume in an aqueous solution, *b* the boiling-point, *c* the percentage of alcohol, and *d* the percentage of water, by volume in the vapour:

a	*b*	*c*	*d*
5	95·9°	35·75	64·25
10	92·6°	51	49
20	88·3°	66·2	33·8
30	85·7°	69·26	30·74
40	84·1°	73·45	26·55
50	82·8°	74·95	24·05
60	81·7°	78·17	21·83
70	80·8°	81·85	18·15
80	79·9°	86·49	13·51
90	79·1°	91·80	8·2
95·57	78·15°	95·57	4·43
97·6	78·4°	97·6	2·4

the higher alcohols also give mixtures with water which boil at lower temperatures than the corresponding pure alcohols. If benzene is mixed with alcohol, the latter may be obtained pure, since a mixture of water and benzene first distils over, then alcohol (at 64·8°), then alcohol and benzene (68·2°), and finally pure alcohol.

Usually absolute alcohol is obtained by distilling the ordinary 90 to 96 per cent. alcohol over calcined potassium carbonate or over anhydrous (*i. e.*, calcined) copper sulphate, redistilling over lime, and finally over baryta or a little sodium or calcium; or it may be left over powdered aluminium until hydrogen ceases to be evolved. The aldehydes of the alcohol may be separated by boiling with 5 per cent. of caustic soda.

If alcohol contains a little water, it becomes turbid when mixed with benzene, carbon disulphide, or paraffin oil, and turns white, calcined copper sulphate blue, and barium hydroxide is precipitated on addition of baryta, the latter dissolving only in the absolute alcohol.

A mixture of 53·9 vols. of alcohol with 49·8 of water gives 100 vols., the contraction of 3·7 per cent. being due to the formation of a labile compound, $(C_2H_5 \cdot OH)_{18}, H_2O$ (or $2H_2O$, etc.). It is a good solvent for resins, oils, colouring-matters, varnishes, ethereal essences, and many other substances, and dissolves sulphur and phosphorus to a slight extent; it coagulates proteins and diffuses through porous membranes more rapidly than water. It dissolves and gelatinises soaps.[1]

It unites with various salts and alkalis as alcohol of crystallisation (KOH, LiCl, $CaCl_2$, $MgCl_2$) (*see* p. 128).

It oxidises easily, giving aldehyde and acetic acid, *e. g.*, with potassium dichromate, MnO_2, or even H_2SO_4, or oxygen in presence of platinum, or with micro-organisms if the solution is dilute. With concentrated nitric acid, it gives various oxidation products and with the dilute acid, glycollic acid. Alcoholic solutions of caustic alkalis turn brown, since they are partially resinified by the aldehyde which forms first and which acts as a reducing agent. Chlorine gives acetaldehyde and various intermediate chlorinated products. In a red-hot tube it decomposes, giving hydrogen and large proportions of hydrocarbons and acids. With sodium it gives *sodium ethoxide* in the form of a white powder (*see later*).

Absolute alcohol, which plays an important part in organic syntheses, is poisonous and rapidly produces death when injected into the blood. It is a powerful antiseptic, especially at 70 per cent. concentration, which most readily coagulates protoplasm and proteins.

The complete combustion of 1 kilo of pure alcohol ($C_2H_5 \cdot OH + 6O = 2CO_2 + 3H_2O$) generates 7193 Cals. and 96 per cent. alcohol, about 6750 Cals.

Alcohol may be detected even in traces (1 : 2000) by means of *Lieben's iodoform reaction* (*see* pp. 121 and 129). This reaction is also given by acetone, isopropyl alcohol, and the aldehydes; according to Buchner (1905) it is preferable to heat the alcoholic liquid with a little paranitrobenzoyl chloride, which forms crystals of ethyl paranitrobenzoate, $NO_2 \cdot C_6H_4 \cdot CO_2C_2H_5$, m.-pt. 57°. In *Rimini's reaction*, the liquid is heated with sulphuric acid and a dilute solution of potassium dichromate : the green colour of the solution and the odour of acetaldehyde are sufficiently characteristic, but the reaction may

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[1] **Solid Alcohol** is nothing but a soapy mass formed from about 20 per cent. of water, 20 per cent. of soap (sodium stearate), and 60 per cent. or more of alcohol; it burns like liquid alcohol, but leaves a residue.

A richer product may be prepared by heating and stirring 100 parts of 96 per cent. alcohol at 60°, dissolving 1 part of stearine and adding 0·5 part of a 30 per cent. aqueous sodium hydroxide solution—just sufficient to make it redden phenolphthalein. Some use a sodium soap charged with silicate (500 per cent.). A solid alcohol that burns without leaving a residue may be obtained by dissolving 20 to 40 parts of collodion in 100 parts of alcohol; others add, instead, 25 parts of a 25 per cent. solution of cellulose acetate in acetic acid, and shake, the crust of solid alcohol which separates being squeezed out.

be confirmed by distilling a few drops of the liquid and treating the distillate with a little sodium nitroprusside and a drop of piperidine, a beautiful blue coloration being obtained if acetaldehyde is present.

The manufacture of alcohol became one of the great chemical industries when a scientific explanation was obtained of the phenomena governing the transformation of starch and sugar. Fermentation, although known from the most ancient times, remained unexplained up to the nineteenth century, and it is solely, or largely, owing to the studies of Caignard de Latour and Schwann, Turpin, Schroeder, Liebig, Pasteur, Nägeli, Cohn, de Bary, and, more recently, Duclaux, Buchner, etc., that the phenomena of *fermentation* are now completely explained and rationally regulated.

In 1836 Caignard de Latour and Schwann found that the fermentation of wine and beer is strictly dependent on the germination of microscopic fungi which multiply in the must or wort. Turpin supposed that these fungi are nourished by the sugar, producing, as the excreta of their vital action, alcohol and carbon dioxide. In 1838 Liebig held that this transformation of sugar is caused by a special intermolecular movement due to substances contained in the ferment itself (microscopic fungus).

Pasteur, in 1872, showed that certain ferments that live at the expense of the oxygen of the air and can decompose sugar into water and carbon dioxide, when they are immersed in saccharine liquids, being no longer able to assimilate oxygen from the air, extract it from the sugar, resolving the molecule of the latter into alcohol and carbon dioxide. Although Nägeli, in 1879, had attempted to reconcile the hypotheses of Liebig and Pasteur, yet up to a few years ago all fermentative phenomena were interpreted on the basis of the ideas enunciated by Pasteur. Progress in the fermentation industry proceeded, *pari passu*, with that of bacteriology.[1]

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[1] **Bacteriology** is the science which studies morphologically and biologically the very small, unicellular, vegetable organisms which are propagated with immense rapidity by *segmentation*. The cell is formed, as in the higher organisms, of an extremely thin *membrane* which permits all the osmotic phenomena (*see* Vol. I., p. 80), and encloses the *protoplasm* in which no central nucleus is visible, but in which there occur scattered granules (of starch and other substances), fat globules, vacuoles containing cell-sap, and sometimes crystals (*e. g.*, of sulphur), while in certain bacteria the protoplasm holds various colouring-matters in solution. The temperature most favourable to their vitality varies, according to the species, from 5° to 40°; they live, however, in a latent condition, at very low temperatures, although they do not reproduce, and they usually die at about 70° (excepting the spores, *see below*). As, in general, they do not contain chlorophyll, they are nourished by complex organic substances already elaborated by other organisms and hence soluble or capable of being rendered soluble (sugars, organic and inorganic ammonium salts, etc.); in this they are clearly differentiated from vegetable organisms and approximate more to the animals. Nutrient matter for bacteria always contains phosphorus, sulphur, potassium, and calcium, and, in certain cases, magnesium and manganese. They are able to take the carbon they require for their nutrition even from ethyl alcohol in a concentration of 4 per cent. (180 species of bacteria are capable of such assimilation) or from methyl alcohol at the same concentration (25 species), and the nitrogen also from inorganic ammonium salts, nitrates, urea, and even free ammonia, the nutriment being made up with mineral substances, such as monopotassium phosphate, magnesium sulphate, etc. (*e. g.*, *Epicoccum purpurescens* requires nitrates and magnesium salts for the formation of its purple colouring matter, while *Aspergillus niger* requires manganese salts, etc.). All bacteria live well and reproduce rapidly in meat-broth or nutrient gelatine. They tolerate more easily alkaline than acid media, and *direct* sunlight kills many species of bacteria, even pathogenic ones. As a result of their vital actions, substances are sometimes formed which kill the bacteria themselves. Different antiseptics have various actions on different bacteria, or else only a specific action on certain of them. The *reproduction* of bacteria takes place ordinarily by *segmentation*, that is, when the cell has reached a certain length a thin wall forms in the middle and divides the cell into two new ones; these divide, in their turn, so that the reproduction of these organisms, which increase in geometrical proportion (1, 2, 4, 8, 16, 32, etc.), proceeds with prodigious rapidity and yields millions of individuals in a few hours. The universal distribution of bacteria is thus easily understood. When the vital conditions are rendered abnormal or difficult for bacteria, in many of them there occurs a contraction of their protoplasm into a more compact mass (at the centre or laterally, according to the species), which forms a separate individual, the *spore*, much more resistant to cold (− 180°) and heat (130° to 140°), and even to antiseptics than the corresponding bacterial cell; the spores can retain life even for some years. Under favourable conditions, the spore breaks its envelope and gives a cell which reproduces by segmentation like the original one. Only certain rare species of bacteria are provided with chlorophyll or other colouring-matters capable of assimilating carbon dioxide under the action of sunlight.

These micro-organisms, termed *bacteria* or *schizomycetes* or *microbes*, are those which produce

During recent times, however, new facts have been discovered which have profoundly shaken the fundamental basis of this theory, according to which no fermentation is possible, except in the presence of certain species of *living* micro-organisms. In reality certain special fermentations are already known which are produced by *enzymes*, *i. e.*, substances of complex chemical compositions which do not manifest anything of the nature of living micro-organisms; for example, *diastase* transforms starch into maltose: $2(C_6H_{10}O_5)_x + H_2O = xC_{12}H_{22}O_{11}$.[1]

Between 1896 and 1900 Buchner succeeded in showing, by careful experiment, that some of these fermentations, which in the past could be induced only by the living micro-organisms, may be effected also by using the *extract* of the bacteria obtained by squeezing out, under great pressure, through special unglazed porcelain filters, the extract of the

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putrefaction and infectious diseases (cholera, carbuncles, typhus, tuberculosis, small-pox, diphtheria, etc.); they are classified, according *to their form*, into: (1) **Desmobacteria** (*bacillus* or vibrio forms like small rods); (2) **Spherobacteria** (*cocci* and *micrococci* of spherical shape and termed *diplococci* if united in twos, *staphylocci* if joined in bunches, and *streptococci* if in strings); (3) **Spirobacteria** (*spirilla* of twisted shape). To give a concrete idea of their forms de Bary described them as analogous to a pencil, a billiard ball, and a corkscrew.

On the basis of their different activities and physiological properties Cohn divided all the species of bacteria into three characteristic groups: (1) *zymogenic*, or those which produce all the non-alcoholic fermentations; (2) *chromogenic*, which produce various colouring-matters (red, violet, yellow, etc.); (3) *pathogenic*, which cause diseases of man and animals. To recognise the latter—given the difficulty of distinguishing them morphologically under the microscope, since different species often have the same form and the same species sometimes several forms—they are inoculated into the blood of living rabbits, rats, guinea-pigs, etc., the pathogenic character being deduced from the effects produced in the animals in two or three days, or sometimes even after a few hours.

The lesser diameter (width) of these unicellular bacteria measures a few tenths of a *micron* (1 micron or $\mu = 0{\cdot}001$ mm.), and in rare cases, as much as $1{\cdot}7\ \mu$; the greater diameter (length) is usually several microns.

If we wish to indicate bacteria in a wider sense of the term, and not to limit them to the *pathogenic* or *saprophytic* (non-pathogenic), but still to those that produce all putrefactions and widen the limits of their dimensions, we may logically divide these micro-organisms into two other groups of similar beings, namely, the **Hyphomycetes** (*moulds*) and the **Blastomycetes** (*ferments*).

The *Hyphomycetes* form groups of branched filaments (*mycelia*), which often subdivide into portions similar to bacteria, but the width of these always exceeds 2μ and often 5μ; they multiply by means of spores and four principal species are distinguished according to the mode of formation of these spores (*conidia*): (1) the *Aspergillus* species, which form, at the extremities of the fruit-bearing filaments (*spore-bearing hyphæ*), a swelling in the form of a club covered with series of spores attached by means of intermediate *sterigmata*; (2) the *Mucor* species (or *Mucedineæ*), in which the spore-bearing hyphæ which start from the mass of mycelia carry *sporangia* (species of capsule) in which the spores develop; (3) the *Oidium* species in which the spores are formed directly in the spore-bearing hyphæ without any special organ of fructification; (4) the *Penicillium* species, which is very common and has branched spore-bearing hyphæ in the form of a brush containing rows of spores. *Aspergillus* and *Oidium* are, however, not separate species, but special sporifying forms of *Eurotium* and *Erysiphæ* belonging to the order of *Ascomycetes*.

The most important of these micro-organisms for industrial purposes are the *Blastomycetes*, *i. e.*, the ferments or unicellular fungi which usually multiply by gemmation (budding), that is, by excrescences forming on the cells and becoming detached when they have reached a certain size, forming new cells which live independently of the mother-cells; under abnormal conditions, however, the ferments multiply also by means of spores, four nuclei being usually formed inside the cell, these then becoming covered with membranes and dividing the mother-cell into four parts forming four new cells.

The cells of the ferments have often a magnitude greater than 5μ, and the most important for alcoholic fermentation form the family of the *Saccharomycetes* (*see later*).

The extraordinary beneficial influence of the bacteria and ferments in nature (apart from the pathogenic action of certain of them on some of the higher organisms) is manifested in the wonderful destructive activity they exert on the refuse and remains of all the higher organisms, converting the complex substances composing them into continually more simple substances until they give CO_2, H_2O, NH_3, and HNO_3. These are the simplest materials which can be used by vegetable organisms to recommence the life-cycle, since in nature nothing is destroyed or created, but everything is transformed and thus life itself rendered eternal.

[1] *Starch*, which is formed in the green leaves of plants under the action of sunlight and of *chlorophyll*, although an insoluble substance and very resistant to various reagents, migrater during the night and accumulates in the seeds, roots (tubers), medulla, etc. We can, however, stop the starch in its path, and can explain how it may be transported by the juices into othes parts of the plant. In fact, various enzymes occur distributed through plants, and among these is *diastase* or *amylase*, which renders the starch soluble by transforming it into soluble (and hence transportable by the juices) sugar (maltose), to be regenerated by an inverse process—unknown to us—in the form of insoluble starch in other parts of the plant.

ferment-cells previously ground with quartz-sand. In this way *Saccharomyces cerevisiæ* (Fig. 117) yields *maltase* (an enzyme occurring also in germinating barley or maize and contained in *Saccharomyces octosporus*), which hydrolyses maltose, transforming it into glucose; from beer-yeast is obtained *invertase* (or *invertin*) capable of resolving saccharose or cane-sugar (not directly fermentable) into fructose and glucose (fermentable); fresh yeast cells yield *zymase*, the enzyme capable of effecting the alcoholic fermentation of various six-carbon-atom sugars (glucose, fructose, etc.).

The action of the enzyme cannot be attributed to the still living protoplasm derived from the cells of the ferment, since the protoplasm may easily be killed in a mixture of alcohol and ether, and after this treatment the enzyme retains its activity. The action of ferments is hence due to the enzymes that they are able to produce, rather than to the biological phenomena of the life of the organisms.

Numerous enzymes are now known which are of great importance in many vital functions of vegetable and animal organisms. It is not certain if the enzymes, with their large and complex molecules, are true proteins, since up to the present they have not been obtained chemically pure; all of them contain nitrogen, but, as they are purified more and more, the nitrogen content continually diminishes and to-day it is held by some that the composition of each enzyme approaches that of the substance it transforms; thus diastase would be a substance similar to starch and poor in nitrogen, whilst the enzymes that transform the proteins would be of true protein nature. *Proteolytic* (decomposition of proteins) and fermentative actions occur only between certain limits of temperature (0° and 65°) and are retarded or prevented by certain poisons (*e. g.*, by traces of prussic acid or by metallic salts that act on proteins, like $HgCl_2$, etc., although they are more, and sometimes completely, resistant to the action of antiseptics that kill ferments, such as salicylic acid, boric acid, ether, etc.). The various enzymes produce one or other of the following general reactions: *hydrolysis* (amylases, sucrases), *coagulation* (enzyme of rennet), *decomposition* (zymase of alcoholic fermentation), *oxidation* (laccase oxidises the juice of the lac-tree), etc. Enzymes exhibit different behaviour towards the stereoisomerides of certain hydrolysable and fermentable substances (*see* section on Sugars).[1]

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[1] The following are some of the more important enzymes :

Diastase (or *amylase*) occurs abundantly in malt (germinating cereals), but is found also in plants, the pancreas, the saliva, the liver, the bile, the blood, the kidneys, and the mucous membrane of the stomach and of the intestines; it transforms starch into maltose and dextrin.

Maltase transforms maltose into glucose, and is found in malt, in *Saccharomyces cerevisiæ*, and in plants and animals.

Zymase causes alcoholic fermentation of glucose, and is contained in yeast and the alcoholic ferments (*Saccharomyces*).

Lactase decomposes milk-sugar.

Melibiase resolves raffinose (or cane-sugar) into molecules of more simple sugars.

Invertase (*sucrase, saccharase*, or *invertin*) decomposes saccharose into glucose and levulose, and is obtained from beer-yeast.

Cytase or **Cellase** attacks cellulose.

Maltodextrinase ferments maltodextrin.

Dextrinase ferments dextrins.

Peptase governs the important digestive functions of the stomach, and peptonises proteins.

Tryptase is found in the pancreas and contributes to the peptonisation and decomposition of the proteins.

Lipase is also found in the pancreas and renders the fats soluble (hydrolyses them).

Emulsin, contained in bitter almonds, and capable of decomposing amygdalin.

Ptyalin is contained in the saliva and initiates the digestion of starchy foods.

Reductase is capable of effecting reduction phenomena, especially in presence of aldehydes, and is hence also known as *aldehydo-catalase ;* it decolorises *Schardinger's reagent* (mixture of methylene blue and formalin). Reductase is widespread in the animal kingdom and occurs in *unboiled milk* (boiled milk is detected by the lack of this enzyme; it does not decompose water or decolorise guaiacol).

The **Oxydases** form a group of enzymes (*laccase, tyrosinase, œnoxydase, catalase*, etc.) capable of effecting oxidations by fixing the free oxygen of the air and transferring it, in the nascent

Still more interesting is the fact that during an ordinary fermentation the amount of sugar fermented does not depend closely on the quantity of living ferment or enzyme; thus large quantities of sugar can be decomposed by small quantities of ferment or enzyme.

The action of the enzymes and of the ferments may be logically compared with that

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state, to the substances to be oxidised. They occur widespread in the vegetable kingdom and are also found in the animal kingdom, and their oxidising action is comparable with that of platinum black (catalyst). In fact the *catalase* found in the blood is capable of decomposing H_2O_2, giving nascent oxygen and water (Loew, 1901). It is now found that the oxydases are formed of mixtures of *oxygenase* and *peroxydase*. Euler and Bolin (1909) obtained a laccase of the *Medicago* type in a chemically pure state, and found it to be composed of calcium salts and a small amount of iron salts of mono-, di-, and tri-basic hydroxy-acids, especially citric, malic, mesoxalic, and glycollic acids.

Peroxydases and Oxygenases. Schönbein (1856) had observed that certain vegetable and animal organisms contain substances analogous to ferments and capable of *decomposing* hydrogen peroxide catalytically with liberation of oxygen, and also of accelerating catalytically this decomposition (*i. e.*, the oxidising action) in the same way that ferrous sulphate does. Loew (1901) showed that the first action is due to a special enzyme, *catalase* (*oxygenase*). Linossier, in 1898, succeeded in separating from pus an enzyme free from oxydase (oxygenase), yet capable of *accelerating* but not of initiating the decomposition of hydrogen peroxide; this he called *peroxydase.* The oxydases and peroxydases often occur together and they may be separated by heating the mixture to 70°, the oxydase being thus killed, or, as was proposed by Aso of Tokio (1902), by dissolving the peroxydase in alcohol which does not dissolve the oxydase, or by poisoning the latter with sodium fluoride or fluosilicate. There are also several plants that contain only peroxydases, among them pumpkins and horse-radish roots (Bach and Chodat, 1903, 1906).

The peroxydases are nitrogenous but non-protein substances, and, when heated with $NaOH$ give NH_3; they always contain about 6 per cent. of ash, 0·8 to 1·4 per cent. being aluminium and 0·2 to 0·6 per cent. manganese. The peroxydases dialyse, whilst the oxygenases do not. The specific action of the peroxydases consists in *activating* in a remarkable manner the oxidising action of H_2O_2 on organic substances, *e. g.*, gallic acid, pyrogallol, etc.; they activate also the action of the peroxides that form in organic substances by the action of the oxygen of the air (*e. g.*, ethereal oils, turpentine, etc.).

In 1897 Bertrand introduced the following hypothesis to explain the action of the oxydases: the latter are regarded as hydrolysable manganese protein compounds, in which the manganese, in the manganous condition, is the transmitter of oxygen from the air to the oxidisable substance; the manganese dioxide formed would then be again reduced by the protein acid radical, the original manganous protein compound being regenerated. Bach and Chodat have, however, found manganese in the peroxydases, although these are not direct oxidising agents.

The peroxydases have no oxidising action, unless a peroxide is present. They do not turn fresh guaiacol tincture blue, but after some hours this change does occur, the tincture having formed peroxide, which may be detected by starch and potassium iodide solution. Whilst the peroxydases accelerate the decomposition of very dilute H_2O_2, this destroys them if concentrated. In 1908 J. Wolff obtained the reactions of the peroxydases by traces of ferrous sulphate or copper sulphate. The oxidising action of the oxygenases (which have, however, not yet been obtained free from peroxydases, although the latter are known free from oxygenases) is only weak and is strongly activated by addition of peroxydase. On the other hand, it seems established that there are two species of peroxydases existing, the one activating strongly the oxygenases and feebly the decomposition of H_2O_2, and the other behaving in the opposite way. The character of the oxydases themselves is indicated by the specific action of one or the other species of peroxydase. Indeed, Bertrand had in 1896 extracted from certain plants, *e. g.*, young potato tubers, an oxydase which differed from all others in not oxidising phenols or the aromatic amines, whilst it oxidised and blackened tyrosine, which is not altered by the ordinary oxydases or even by H_2O_2 combined with one of the ordinary peroxydases. Bach (1906) succeeded in separating the specific peroxydase from tyrosinase and in showing that this peroxydase is capable of causing the oxidation of tyrosine only when mixed with the corresponding oxygenase or in presence of H_2O_2 alone. Hence the action of tyrosinase is due to the specific action of its peroxydase. Bach holds further that in the phenomena of respiration of organisms, oxidation due to oxydases plays no part, since this leads to true condensations, to syntheses of more complex products; for respiratory phenomena there should exist enzymes of a type not yet known and capable of decomposing and oxidising the reserve materials of the organism (fats, carbohydrates, etc., which are not oxidised by oxydases).

At the present day the catalytic action of the enzymes is explained as due to small quantities of metals which they contain; thus the important action of the *hæmoglobin* of the blood (which fixes the oxygen in the lungs in a labile condition and transports it to all parts of the organism) appears to be due to the small quantities of iron present, this inducing the decomposition of the food materials; further, the synthetic action of the peroxydases is perhaps due to the manganese they contain (*see above*), just as the important synthetic functions of chlorophyll, according to Willstätter's recent work, appears to be owing to the magnesium present in it. Recently (1910) Bach has, however, succeeded in preparing very active oxydases and peroxydases free from iron and manganese, so that the true explanation of the activity of these enzymes remains to be discovered.

of the *inorganic catalysts* (Vol. I., pp. 71, 319), which only produce an enormous increase in the velocity of reaction, in our case, of the decomposition of sugar. That these *organic catalysts* have an action really similar to that of the inorganic catalysts can be shown by certain other interesting facts.

Some years ago Duclaux succeeded in producing alcoholic fermentation by dilute alkali; Traube in 1899 transformed sugar into alcohol by means of finely divided platinum alone at 160°; while Schade in 1906 converted an alkaline solution of glucose, in absence of enzyme, quantitatively into acetaldehyde and formic acid ($C_6H_{12}O_6 = 2C_2H_4O + 2CH_2O_2$), and these products, under the catalytic influence of *rhodium*, are transformed quantitatively into CO_2 and alcohol (perhaps the formic acid first gives CO_2 and H_2, the latter, in the nascent state, reducing the aldehyde to alcohol).[1]

Further, in chemical equilibria (Vol. I., p. 64), the action of catalysts in reversible reactions is regulated by the temperature and concentration conditions, and the same phenomenon is met with in the case of enzymes : indeed, when diastase has converted a certain quantity (dependent on the temperature) of starch into maltose, the hydrolytic change is arrested (*i. e.*, equilibrium is reached in the reversible reaction : starch $\leftrightarrows$ maltose); if, however, part of the maltose is fermented into alcohol and CO_2, the equilibrium is disturbed and the diastase hydrolyses a further quantity of starch. Also at temperatures above 55°, diastase forms dextrin in preference to maltose. An analogous phenomenon is observed in the hydrolysis of *amygdalin* by emulsin. It has already been mentioned that maltase transforms maltose first into glucose, but when a certain proportion between these two products is reached, the hydrolysis ceases owing to equilibrium being attained : $C_{12}H_{22}O_{11} + H_2O \leftrightarrows 2C_6H_{12}O_6$, and the transformation proceeds further only when the glucose is removed by alcoholic fermentation; Emmerling has realised the inverse reaction by displacing the equilibrium by addition of glucose (in which case *isomaltose* is produced).

Also in the action of maltase on amygdalin, Emmerling succeeded in producing the reverse reaction, and at the St. Louis Exhibition in 1904 he showed a fine specimen of amygdalin prepared synthetically by an enzymic process.[2]

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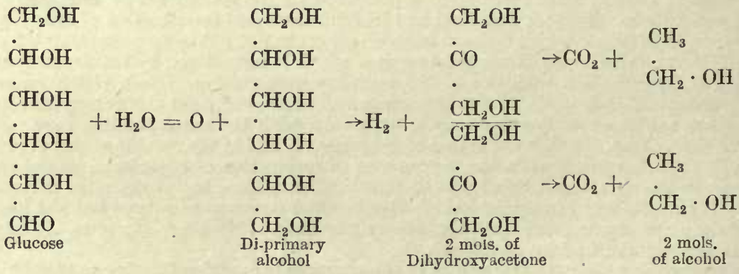
[1] Buchner and Meisenheimer (1909) explain the action of ferments, from the chemical point of view, by the addition of a molecule of water to the sugar and abstraction of an atom of oxygen by the ferment, so that there results, as an unstable intermediate product, a di-primary alcohol, which, in its turn, is immediately decomposed into H_2 and 2 mols. of dihydroxyacetone; the last product is able to decompose into CO_2 and alcohol, while the hydrogen continues to transform fresh quantities of sugar into the dihydric alcohol, and so on. Boysen-Jensen (1909) finds that the reactions for dihydroxyacetone are given by fermentations; the decomposition would hence take place thus :



$$\underset{\text{Glucose}}{\begin{array}{c}CH_2OH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CHO\end{array}} + H_2O = O + \underset{\text{Di-primary alcohol}}{\begin{array}{c}CH_2OH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CHOH\\ \cdot\\ CH_2OH\end{array}} \rightarrow H_2 + \underset{\text{2 mols. of Dihydroxyacetone}}{\begin{array}{c}CH_2OH\\ \cdot\\ CO\\ \cdot\\ CH_2OH\\ \hline CH_2OH\\ \cdot\\ CO\\ \cdot\\ CH_2OH\end{array}} \begin{array}{l}\rightarrow CO_2 +\\ \\ \\ \rightarrow CO_2 +\end{array} \underset{\text{2 mols. of alcohol}}{\begin{array}{c}CH_3\\ \cdot\\ CH_2\cdot OH\\ \\ CH_3\\ \cdot\\ CH_2\cdot OH\end{array}}$$

[2] $$\underset{\text{Glucoside of phenylglycollic nitrile}}{C_6H_5\cdot CH(CN)\cdot C_6H_{11}O_6} + C_6H_{12}O_6 \underset{\text{Maltase}}{\rightleftarrows} \underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + H_2O$$

or, more completely :

$$\underset{\text{Glucose}}{2C_6H_{12}O_6} + \underset{\text{Hydrocyanic acid}}{HCN} + \underset{\text{Benzaldehyde}}{C_6H_5\cdot CHO} \rightleftarrows 2H_2O + 2_{20}H_{27}NO_{11}$$

Franzen and Steppuhn (1911) have shown experimentally that, in the enzymic conversion of sugar into alcohol and carbon dioxide, formic acid is produced as an intermediate product.

So that with one and the same enzyme, analytic and synthetic processes can be effected. Cremer obtained *glycogen* $(C_6H_{10}O_5)_y$ from levulose $(C_6H_{12}O_6)$ by means of an extract of yeast, and Hanriot, Kastle, and Loevenhart prepared monobutyrin and butyl acetate synthetically by means of *lipase.* The enzymes also effect the so-called *asymmetric syntheses*, *i. e.*, they give *optically active* compounds containing asymmetric carbon (1908).

Also of interest is the fact that a single ferment may contain various enzymes; thus, from *Saccharomyces cerevisiæ*, maltase and invertase may be extracted easily and also zymase, though with more difficulty (by grinding the yeast with powdered quartz and forcing the extract through a porcelain filter under high pressure).

These recent discoveries on the reversibility of the reactions effected by enzymes are of great importance, as it was at first thought that enzymes or ferments in general were capable of causing only decompositions and not synthetic reactions, whereas their analogy with inorganic ferments is now complete. The discoveries are all the more remarkable, since the same phenomenon of vitality—in the single cell as in more complex organisms—may be reduced to an enzymic phenomenon; that is to say, the exchange of material in the organism (decomposition, recomposition, growth) takes place by means of these organic catalysts, which cause the decomposition of food, preparing various complex materials which form the organism itself, and at the same time generating the energy manifested in the *vitality*, enzymic phenomena being always exothermic. This hypothesis may, with advantage, be substituted for the too abstract *biogen* [1] hypothesis, to explain vital phenomena.

This result is in harmony with Wohl and Schade's theory, according to which sugar when fermented passes through various intermediate products, especially lactic acid, this in its turn, being resolved into acetaldehyde and formic acid; the latter would then give carbon dioxide and hydrogen, the nascent hydrogen transforming the acetaldehyde into ethyl alcohol (*see* Note, p. 136).

Similar phenomena were observed by Neuberg and Kerb (1913). Thus, by the action of enzymes, pyruvic acid $(CH_3 \cdot CO \cdot CO_2H)$ is transformed readily and completely into CO_2 and acetaldehyde, with simultaneous formation of ethyl alcohol (this is facilitated by presence of glycerol), probably from the aldehyde. Further, to the extent of 85 per cent. butyraldehyde and valeraldehyde are converted by enzymes into the corresponding alcohols and α-ketobutyric acid into propyl alcohol.

[1] **Hypotheses of Biogen, Toxins, and Genesis of Life.** The physical and physiological basis of life resides especially in the *protoplasm*, the semi-fluid, almost always colourless, refractive substance—insoluble in water—which everywhere constitutes the essential part of the cell. Protoplasm is formed principally of protein substances, whilst it is thought that the fats and carbohydrates are not *active* components. To the protoplasm is attributed the fundamental property of vitality, *i. e.*, the exchange of material, but it is not known how its components—the proteins—can have such properties or in what physico-chemical aggregation of the proteins (the plastidules and bionomads are regarded as morphological components or units of protoplasm) they have their origin.

In animals one of the principal functions of the *blood* is that of supplying the respiratory needs of the tissues in virtue of the *hæmoglobin* contained in the blood of vertebrates [besides *fibrinogen*, *serum-albumin*, and *paraglobulin*; whilst with the invertebrates there are *echinochrom*, *chlorocruorin*, *hæmoerythrin*, *hæmocyanin* (containing copper), and *pinnoglobin* (containing manganese), which have the same functions as hæmoglobin]; it is formed of a protein substance united with a ferruginous compound, which takes up oxygen at the respiratory surfaces of the organism (skin, bronchi, and lungs), and brings it into close contact with the tissues.

The vital processes of the organism being due to the exchange of material in the cells full of protoplasm, the *biogenic hypothesis* assumes that this is brought about by a very complex, labile compound, which, by being continually decomposed and reconstituted, maintains the interchange uninterruptedly. By many this compound is called *living albumin*, but Max Verworn (1895 and 1902) regards this as an unsuitable name, and does not think it has been shown to be a true albuminoid, although it is a nitrogenous substance; there are possibly several substances in a state of labile combination and these he calls *molecules of biogen.*

It has been observed that in organisms, as in parts of them, vitality ceases when oxygen is eliminated, many of them subsequently (the frog even after twenty-five hours) recovering it in presence of oxygen. From this arise two hypotheses: (1) the molecule of biogen becomes labile, and hence gives rise to decompositions and recompositions, that is, to the vital process—since it unites transitorily with oxygen; (2) oxygen serves only to oxidise or eliminate the

In order to ascertain if a given action is due to enzymes or to organised ferments, the liquid is passed under pressure through a Chamberland porous

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decomposition products of the biogen (admittedly labile), and when there is no oxygen, these products are not eliminated, so that the decomposition and recomposition of the biogen are arrested. By experiments on the frog Verworn has shown that the former hypothesis is the more probable.

Since, in the vital process, under the action of oxygen, it is especially the carbon dioxide that is eliminated, often along with lactic acid, water, etc., whilst the elimination of nitrogenous substances does not increase, it may be assumed that biogen is constituted of a benzene nucleus with lateral chains of carbohydrate and aldehydic character and with an oxygen-carrying nitrogenous group which fixes the oxygen of the air (just as NO gives NO_2 in the lead-chambers of sulphuric acid works) and gives it up to the lateral chain, which is oxidised (*Ehrlich's side-chain hypothesis*, 1882–1902) to CO_2, lactic acid, H_2O, etc., these being eliminated; the nitrogenous group, thus reduced, remains united with the benzene group, which, with new food, forms the biogen molecule, this being again decomposed by oxygen and so on. The digested food-materials carry, with the blood, new materials to the regeneration of biogen (without food, death ensues), the oxygen then effecting the changes described above. The seat of the biogen lies in the liquid protoplasm of the cell (not in its nucleus), into which oxygen enters in the state of labile combinations not yet defined, but capable of giving it up when needed: these compounds are more stable in the cold than in the hot, and are those that carry on the vitality during prolonged fasts. These reserve materials are probably formed by the decomposition of the food by means of intracellular enzymes, which form the connecting-link between the living substance (biogen) and the non-living (foods), transforming the latter into the former.

The biogen hypothesis is opposed by that of the enzymes as factors of the vital process and, given the varied nature of the phenomena and of the chemical transformations occurring in the living organism, and the variety of the numerous chemical groups forming a protein molecule, it is perhaps imprudent to refer all these phenomena to a single compound, biogen, when we already know different enzymes which certainly effect well-investigated, definite reactions. From the action of different enzymes on the protein complex forming the protoplasm of the cell, there results the many-sided phenomenon of vitality. In certain cases it is possible to go still further, as it must be admitted that many synthetic and analytic phenomena of organic substances (*e. g.*, the fermentation of sugar) take place even without protoplasm, by the direct action of the enzyme alone (*see* p. 134).

Further, by simple catalytic actions, it is now possible to effect artificial fertilisation (*artificial parthenogenesis*); for example, by treating unfertilised eggs of the sea-urchin with solutions of various chlorides, best of all, magnesium chloride, Loeb (1899 and 1900) obtained living larvæ; Giard (1904) studied the artificial parthenogenesis of the star-fish (*Asteria rubens*); Tichomiroff (1886 and 1902) and, better, Quajat at Padua (1905) obtained partial artificial parthenogenesis of the virgin eggs of the silk-worm.

Most interesting of all are the investigations on *serotherapy* which have led to the most unexpected results when, instead of the observations being limited to the bacteria, the poisonous or beneficial substances which they elaborate or secrete have been considered. These *toxins* or *antitoxins* secreted by bacteria or formed in animal organisms also appear to be enzymes, exhibiting, however, their activity in phenomena of a different and more complex nature.

Since 1902 Arrhenius, in conjunction first with the head of the German school, Ehrlich, and later with that of the Danish school, Madsen, has devoted himself to the interpretation of *serotherapy*, making effectual use of all the modern laws of physical chemistry. He has succeeded in following and controlling the formation and action of toxins and antitoxins in the animal organism by empirical mathematical formulæ, calculated beforehand from the results of previous experiments; it is not improbable that the time will soon arrive when from these empirical formulæ, suitably co-ordinated, rational formulæ will be derived leading to new and important natural laws, from which general pathology will obtain great principles rendering it possible for man and other animals to be immunised against the attacks of pathogenic bacteria. Then, and only then, will man have triumphed over the microbe.

By injecting more or less poisonous substances (*toxins*) into the animal organisms, the so-called *anti-bodies* (*antitoxins*) are formed in the blood, but their formation is probably incomplete in consequence of the laws of chemical equilibria discovered by Guldberg and Waage (Vol. I., p. 65).

The corresponding antitoxins are known for only a few poisons. Those of *solanine* and *saponin* (1901) and of *morphine* (*antimorphine*) (1903) have been sought for in vain by inoculating guinea-pigs and rabbits, so that these three poisons are not to be regarded as toxins. From castor-oil seeds *ricin* has been extracted—a toxin for which the corresponding *antiricin* is known; also, seeds of *Abrus præcatorius* and *Robinia pseudacacia* yield the poisons *abrin* and *robin*, for which the corresponding antitoxins have been obtained. Animals also produce anti-bodies of non-poisonous substances; thus, if any cells whatsoever are injected into the blood, anti-bodies are more or less rapidly produced which have a special destructive action on these cells. Also by injecting *rennet* (which coagulates milk) an *antirennet* is obtained which is able to prevent the coagulating action of the rennet.

From pathogenic bacteria are obtained anti-bodies (by inoculation) to certain proteolytic enzymes: in 1893 Hildebrandt found an anti-body to *emulsin* and Gessard (1901) prepared an anti-body to *tyrosinase* (*see above*); from the serum of a goose inoculated with pepsin, H. Sachs (1902) obtained an *antipepsin;* A. Schütze (1904) obtained *antilactase* by making subcutaneous porcelain filter, which retains the ferment cells, but not the enzymes; the filtered liquid is then examined to ascertain if it still produces the enzymic action. Alternatively, the liquid may be mixed with chloroform, which arrests all cellular life, but does not act on the enzymes.

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and intermuscular inoculations with the lactase of *kephir* (*which see*), and similarly were prepared anti-bodies to *cynarase*, *zymase*, *urease*, and the fibrin and pancreatic ferments.

It is difficult to establish a limit or any essential difference between enzymes or ferments and toxins, and the preparation of anti-bodies to all these active substances is, perhaps, only a matter of time. The anti-bodies are divided into two classes, according as they are obtained by inoculation of homogeneous solutions (toxins) or of emulsions of bacteria or cells (red blood corpuscles), etc. The anti-body formed by the inoculation of a homogeneous solution combines with the toxin of the latter, forming an innocuous substance, which is called an *antitoxin* if soluble or a *precipitin* if insoluble. The injection of bacteria sometimes leads to the formation of anti-bodies capable of *dissolving* the bacteria themselves (from which they are derived) and these anti-bodies are then termed *lysins* (*bacteriolysins*). There may also be formed anti-bodies which agglutinate the inoculated cells, *i. e.*, *agglutinins*, but this depends on the presence of salts. The cholesterin and lecithin of the organism often form part of the toxin or antitoxin. Cholesterin, for example, acts as an antitoxin to *tetanolysin* and other lysins. According to Metchnikoff it is the *leucocytes* (white corpuscles) which produce the antitoxins, but this has not been rigorously proved, although Wright has shown that certain anti-bodies (*opsonins*) exhibit their activity against bacteria only in presence of leucocytes.

That the action between *toxins* and *antitoxins* resembles chemical neutralisation was assumed at the time of the discovery of the first diphtheritic antitoxin by Behring and Kitasato in 1890, and was supported by the German school with Ehrlich at its head. From 1893, however, the French school (Roux, Vaillard, Metchnikoff) and also Buchner held that the antitoxins exert a physiological action, *exciting*, as it were, the organic tissues to resist the attacks of these poisons (toxins). When, however, Ehrlich showed that the agglutinating action of *ricin* on the red blood corpuscles (suspended in physiological serum, that is, in 0·9 per cent. NaCl solution) could be annulled by simply adding *antiricin*, and because he showed that the neutralisation of the action of a given quantity of toxin required the presence of a proportionate amount of antitoxin, most scientific men abandoned the physiological hypothesis. Ehrlich's more recent studies on the action of two arsenical compounds on the toxins have led to the cure of *sleeping-sickness* and probably to that of *syphilis* (by means of the product 606). In suitable conditions of temperature, etc., the original toxins may be regenerated from the antitoxins by a reversible process (Reversible Reactions, Vol. I., p. 66); this was shown by Morgenroth (1905) by dissociating the antitoxin with a little HCl and destroying the anti-body at 100°, thus obtaining the original toxin. So that validity can no longer be ascribed to the hypothesis of Behring (1890), Nernst (1904), and Biltz, Much, and Siebert (1905), according to which the toxins are absorbed by the colloidal antitoxins and then *destroyed*.

The toxins and antitoxins, although colloidal substances, diffuse easily and give osmotic pressures according to van 't Hoff's law.

Toxins diffuse through water and gelatine *much* more rapidly than antitoxins, so that a mixture of the two bodies can be separated into its components. The difference in the rapidity of diffusion depends on the molecular magnitudes (according to E. W. Reid, hæmoglobin has a molecular weight of 48,000). The molecular weights of the antitoxins would be 10 to 100 times as great as those of the toxins.

The velocity of reaction of the different toxins does not depend, as Morgenroth supposed, on catalytic actions, but, as Arrhenius and Madsen showed, on the temperature, and is regulated by a law deduced from thermodynamical considerations based on van 't Hoff's laws of solutions.

A number of other factors of the vitality of the organism—digestion of food, assimilation of carbon dioxide by plants, development of the egg, production of alcohol during the fermentation of sugar, etc.—are due to enzymes or toxins and antitoxins, the actions of which are regulated by the laws of chemical equilibria and of the velocity of reaction, and are perhaps not disconnected from catalytic phenomena or from reactions similar to or identical with those assumed by the biogen and side-chain hypotheses.

Further, the studies of O. Lehmann and of S. Leduc (1896) on **Liquid Crystals**, according to which, under certain conditions, solutions of substances can assume the form of crystals or of cells that grow, multiply, and die, like actual organisms (*see* Vol. I., p. 117), furnish a probable explanation of the transition from organic substances to organised bodies. Thus, after what has been stated above, the entire cycle of the genesis of life can be comprehended, from the transformation of inorganic substances into organic (*see* pp. 1, 35, and 111, and later: Synthetic Alcohol) and of these into organised (or living), by hypotheses based on scientific facts. It still remains, however, to explain the origin of the inorganic world, terrestrial and extra-terrestrial, the answer of science being that, in accordance with Lavoisier's law, nothing is created and nothing destroyed, so that the inorganic world has always existed and is eternal, and eternal also is its continuous evolution. This is the actual limit of human knowledge, which, in its imperfection, cannot explain the infinite and the eternal. No metaphysical philosophy has succeeded in obtaining a final clue to this secret of eternity, since it is not a plausible or even rational explanation to refer the eternity of the inorganic world to a hypothetical, abstract, supernatural being who created everything from nothing, in contradiction to the fundamental laws of positive science, the first of all of these being those of the conservation of mass and of energy.

A liquid containing an enzyme is coloured blue by the addition of an alcoholic solution of guaiacum resin, previously mixed with a drop of hydrogen peroxide.

The enzymes are, as a rule, destroyed by boiling.

During recent years numerous experiments have been made on fermentation by means of filtered extracts of ferments free from cells. The components of such extracts have been studied in various ways and attempts made to precipitate fractionally various enzymes (*e. g.*, by acetone or colloidal ferric hydroxide); most of these precipitates lose, however, much of their fermentative power, and for the latter to be a maximum a necessary condition seems to be the presence of the *co-enzyme*, which may be separated from the enzyme by fractional precipitation. According to Ivanoff (1910) alcoholic fermentation by means of zymase appears to take place in three phases: (1) depolymerisation of the glucose; (2) the action of a soluble co-enzyme, *syntase*, yielding a phospho-organic compound (compound of phosphoric acid with a triose resulting from the depolymerisation mentioned), (*see* notes on pp. 136 and 147), and (3) resolution of the phospho-organic compound with generation of alcohol, by the action of *alcoholase* (slightly soluble co-enzyme of zymase).

Since 1899 various attempts have been made to extract enzymes from fresh yeast (containing 75 per cent. of water) by *plasmolysis* with solutions of salts or glycerine or in presence of chloroform, etc. (Lintner, Hahn, De Meulmestre, Rinckleben, van Laar), for twenty to thirty hours at 25°, but liquids of little activity were thus obtained. A. von Lebedeff (1912) obtains better results by simple maceration for two hours at 35° or for six hours at 25°, and if either co-enzyme concentrated in a vacuum or disodium phosphate is added to the liquid thus obtained, a highly active fermenting medium is produced. The maceration method may be applied also to yeast dried at 15°.[1]

A number of attempts have been made, without marked success, to prepare enzymes by chemical means away from, and independently of yeast cells. However, A. D. Bar (U.S. Pat. 1,051,061, applied for in 1909 and granted in 1913) obtains an enzyme of great catalytic activity by molecular scission of protein substances with alkali and acid; thus, pepsin is treated for twenty-four hours with ammonia, and, after removal of the latter, for five days with acetic acid, distillation of the latter then leaving a brown, hygroscopic powder which is soluble in water and insoluble in alcohol, ether, or chloroform, and exhibits very active enzymic properties.

Certain substances exist which increase or enhance the actions of various enzymes; thus, according to Hoyer, Tanaka, Falk, and Hamlin (1913), the inactive zymogen of the lipase of castor-oil seeds is transformed into active enzyme by manganese sulphate, although other oxidising agents give either negative or but slight effects.

INDUSTRIAL PREPARATION OF ALCOHOL. As already mentioned, the prime materials are saccharine or starchy substances; the latter, by the action of enzymes (diastase and maltase), are transformed into maltose and glucose, and then by the action of the zymase contained in yeast-cells (species *Saccharomyces*, *see* pp. 134 and 146) the glucose is transformed, to the extent of 95 per cent., into alcohol and CO_2, with evolution of heat.

The treatment of the starchy materials is carried out as follows: the *starch* is obtained from various prime economic materials, namely, *maize* (especially in Italy, Hungary, and America), *potatoes* (Germany, France, England, and Russia; attempts to introduce the potato industry into Italy have as yet come to nothing); *cereals* (Russia and England); *rice* (England, Japan, China, Italy).

There are two practical processes: (1) the action of dilute mineral acids

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[1] *Diamalt* or *Diastofor*. Of great industrial importance are very active diastases obtained as more or less concentrated extracts of barley malt (*see later*, Beer), these being used as concentrated foods or strengthening agents in cases of chlorosis, bronchitis, incipient phthisis, etc. Large use is made of *diamalt, diastofor*, etc., which are highly concentrated malt extracts employed in the textile industry for dissolving starch and removing the dressing from textile fabrics (*see later*, Textile fibres) and also in baking, the degradation of the starch of the flour which it initiates facilitating the subsequent action of the yeast.

These extracts contain 60 to 70 per cent. of reducing sugars (three-fourths maltose) and 5 to 7 per cent. of nitrogenous substances; they are often adulterated with glucose, dextrin, etc.

in the hot, and (2) the action of certain hydrolytic enzymes (like *diastase* contained in *malt*).

(1) *Transformation of starch by dilute acids.* In this transformation starch yields glucose almost quantitatively: $(C_6H_{10}O_5)_n$ (starch) + $nH_2O = nC_6H_{12}O_6$; we shall deal more in detail with this process later on, in the section on Glucose. At present only the second process will be considered.

(2) *Transformation of starch by means of enzymes.* Of the enzymes, that which is of the most service industrially, is *diastase.* It is formed more especially during the early stages of the germination of cereals (maize, barley, etc.), and this germinated grain forms *malt,* which is most favoured by a temperature of 45° to 55° in its transformation of starch into dextrins [amylodextrin, erythrodextrin, achroödextrin, $(C_{12}H_{20}O_{10})x$] and into maltose and isomaltose, $C_{12}H_{22}O_{11}$.

As has been already mentioned (p. 136), this reaction is regulated by the laws of chemical equilibria, and depends especially on the temperature : between 45° and 50° maltose is preferably formed, and at about 60°, dextrin.

We have already noticed how maltose is transformed into glucose by means of *maltase*, and how the chemical equilibrium is displaced, by gradually transforming the glucose into alcohol by the zymase of the yeast during fermentation.

Of the various malts used industrially, that of barley is the most active, then follow wheat and rye, and, finally, maize; the last-named is one-third less active than that of barley, but owing to its low price has practical advantages, and in Italy is the one most commonly used.

In describing the industry of brewing, we shall deal in detail with the practical manufacture of malt, and we would refer the reader to that section for a description of the preparation of maize malt, which does not differ from that of barley malt.

As regards the use of chlorine dioxide to increase the germinative power of maize, as proposed by Effront, *see* Vol. I., p. 186.

The starchy matters forming the starting materials of the alcohol industry (cereals, potatoes, etc.) cannot be subjected to the action of diastase unless their starch is first transformed into a semi-solution (starch-paste) by treating with water or steam at a high temperature; the starch-granules swell and then burst and readily assimilate water (potato starch at 65°, maize starch at 75°, barley starch at 80°). The materials are hence first macerated or ground, and then extracted with hot water, to be subjected subsequently to saccharification with malt and finally to alcoholic fermentation.

The following Table gives the amounts of starchy and extractive matters per 100 kilos of various materials, together with the theoretical yields of alcohol:

	Starchy and extractive matters	Alcohol
Wheat	65–68 kilos	32–34 kilos
Maize	62–67 „	31–33 „
Barley	63–65 „	30–32 „
Rye	66–69 „	34–35 „
Rice	78–82 „	39–43 „
Durra	61–64 „	30–32 „
Green potatoes . . .	18–20 „	9–10 „
Dry potatoes . . .	68–70 „	34–35 „

In washed potatoes the starch is calculated from their specific gravity (*see later :* Starch).

In cereals and potatoes the content of starch may be determined as follows : 200 grams of potatoes (75 grams of ground cereal) are heated in a flask with 600 c.c. of water and 10 c.c. of hydrochloric acid (sp. gr. 1·2 = 4·7 grams HCl) for ten hours at 90°, the volume made up to 1 litre and 3·5 grams of the HCl neutralised with caustic soda (leaving 1 gram free); the whole is poured into a larger flask, a few grams of beer-yeast being added and the flask kept at 25° for two or three days until the fermentation is over, when half of the liquid is distilled and the alcohol estimated in the distillate by means of the specific gravity. 100 kilos of starch yield practically 63·5 litres of alcohol. This method gives also the yield of alcohol (other methods for the exact determination of starch are given in the chapter on Starch).

The fresh potatoes are washed free from stones and earth in an Eckert mechanical washer (Fig. 105), passing first into a rotating sieve, *E*, which removes the stones and, by means of the blades, *F*, carries the potatoes into the tank, *A*, through which water flows and in which they are stirred by the vanes, *C*, fixed to a rotating axis; the latter is inclined in such a way that the potatoes are gradually forced to the far end of the tank, where a rotating disc, furnished with perforated blades, *G*, collects them and removes them from the tank. A bucket elevator raises them to the opening of a Pauksch's improved form of the conical Henze autoclave (Fig. 106), which is made of sheet-iron, has a volume of 2500 to 3000 litres, and takes about 1500 to 3000 kilos of potatoes; in this they are treated for an hour or more with steam at 2·5 to 3·5 atmos. pressure. Such an apparatus may also be used for treating maize and other cereals, and gives a much denser wort than was previously obtained when steam at 100° was used; in addition, it effects a better dissolution of the starch, and is of advantage to manufacturers in countries where the alcohol tax is based on the volume of wort fermented (or of the fermenting vats). The steam is passed in at the top by the tube *b*, and is distributed uniformly over the interior by means of a perforated pipe (shown dotted at *c*), the tap, *g*, at the bottom being left open to discharge the condensed water. When the whole mass is hot, steam begins to issue from this tap and drives out all the air. The tap is then shut, and the pressure, shown by the manometer, *e*, soon rises to 3 atmos. After about forty-five minutes at this pressure (temperature 135°), the conversion is complete. With damaged or frozen potatoes, the steam is allowed to issue for an hour from the tap, *g*, before raising the pressure, and steam is then passed in by the pipe *b′* as well. A pressure higher than 3 atmos. turns the mass brown, owing to caramelisation of the maltose. To discharge the apparatus, the pressure is maintained at its maximum and connection made with the discharge pipe, *i*, by opening the valve, *h*. At the bottom of the cone, just above *k*, is a horizontal disc of cutting grids, through which the whole of the mass is forced by the steam-pressure and thus converted into a paste; the pipe *i* carries it to the coolers and then to the wort vessels, where suitable stirrers complete the gelatinisation of the mass.

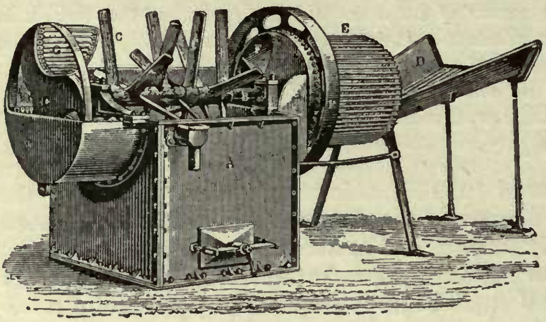

FIG. 105.

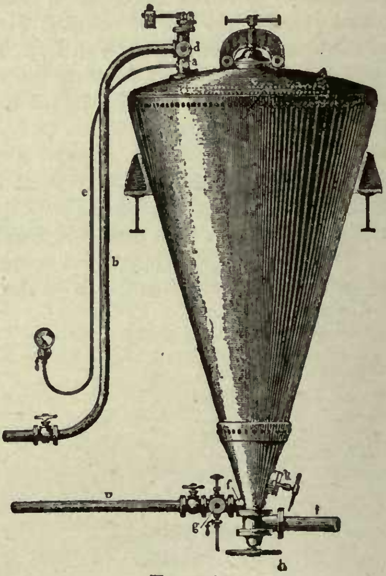

FIG. 106.

In order to avoid danger of explosion, the Henze autoclaves should be tested once a year to ascertain if they are capable of withstanding the pressure employed, since they may become weakened at rusted parts.

Maize, rice, and cereals are also treated in the Henze apparatus, but with the addition of 110 to 140 kilos of water per 100 kilos of cereals, since these contain less water (15 per cent.) than potatoes (75 per cent.), and without the water the desired fluidity of the starch would not be obtained. The volume of the autoclave is 350 litres per 100 kilos of maize. If a pressure of 5 atmos. cannot be easily attained in the autoclave, instead of using the whole grain, it is better to crush or grind it coarsely and then to introduce it into the necessary quantity of boiling water in the autoclave. During the boiling, the maize should be kept in continual motion by steam-jets at the bottom and along the autoclave, or by an air-jet at the bottom with an outlet at the top, so that a spiral motion is imparted to the mass (Fig. 107). Only rarely are mechanical stirrers employed inside the autoclave. After an hour's heating the pressure reaches 2½ atmos. and is raised to 3 atmos. in another hour. The mass is then discharged in the usual way.

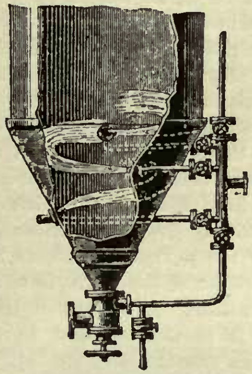
Fig. 107.

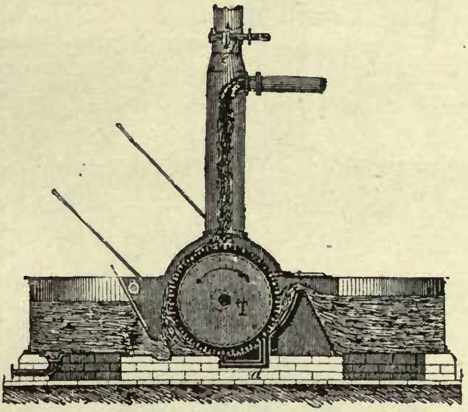

Fig. 108.

Maize that is too dry is steeped in water for a day before boiling.

Maize always contains a little ready-formed sugar (1·7 to 10 per cent.), and this must be allowed for in calculating the yield and also in order to avoid too protracted heating, which caramelises the wort and injures it by decomposing the large proportions of fat present.

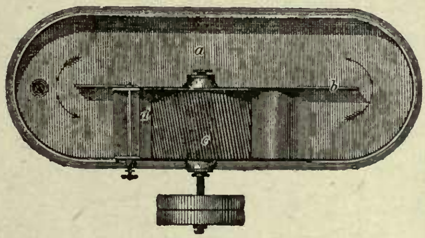

Fig. 109.

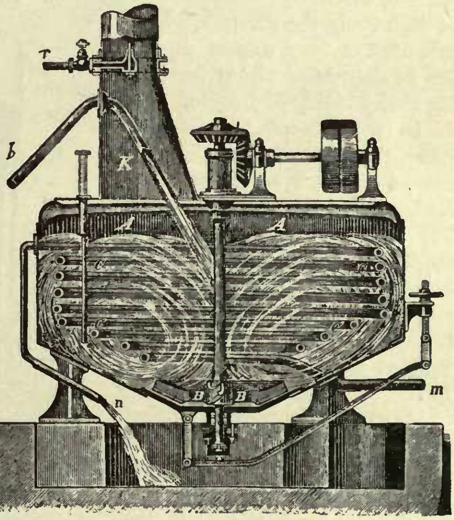

Fig. 110.

Saccharification is effected by means of malt (2·5 to 3 per cent. on the weight of maize) added to the starchy mass at a concentration of about 14° Bé. and cooled to about 50°; if it is too cold, it coagulates and the diastase acts irregularly; at 35° to 40° the lactic fermentation readily takes place; above 65° to 70° the diastase is altered and rendered less active, dextrin being then formed in preference to maltose. The paste from the Henze autoclave is cooled in various ways, *e. g.*, with Ellenberg's apparatus (section, Fig. 108; plan, Fig. 109), in which it is dropped from the top of a pipe into a vessel similar to the hollanders used in paper factories (*see* Paper), where it is mixed, cooled, and broken up by a rotating drum, *T*, fitted with knives which graze other knives fixed to an inclined plate, *d*, at the bottom of the vessel; the drum makes 200 revolutions per minute; above the pipe, *f*, by which the paste enters is a Körting injector, *e*, which produces a strong current of air, and thus facilitates the cooling of the paste during its fall.

At the present time preference is given to apparatus with centrifugal stirrers, the cooling and also the saccharification being carried out in these. Fig. 110 shows the Hentschel apparatus. The hot starch-paste from the Henze converter passes through the pipe *b* into the vessel *A*, where it is cooled by water flowing from *m* to *n* through an internal coil; the mass is mixed by means of a kind of screw, *B*, rotated by bevel-wheels outside the vessel and the air-draught is produced by the Körting injector, *r*. Fig. 111 shows a section of the Pauksch masher, in which the cooling is effected by means of water circulating through the jacket, *C*, surrounding the vessel, the liquid being mixed by four blades, *p*, which are rapidly rotated (300 revolutions per minute) by the pulley, *S*, and, as they graze the bottom of the vessel, have also a grinding action. A battery of Henze autoclaves is sometimes used in conjunction with one masher (Fig. 112).

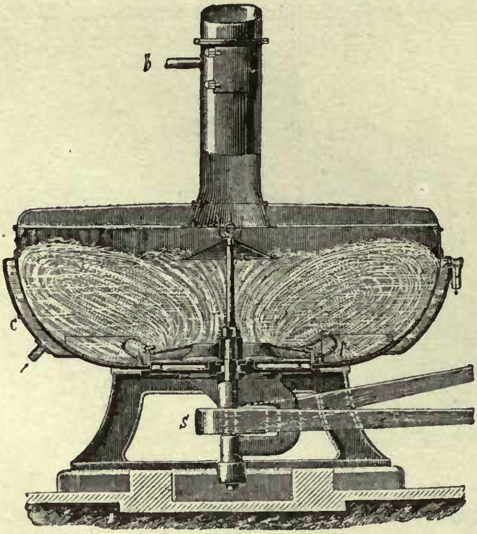

Fig. 111.

Since, during this saccharification, which may last three or four hours (and is complete when a test of the liquid, now very fluid, no longer gives the blue starch reaction with iodine solution), the mass may become infected with extraneous bacteria, which may have a harmful influence during the alcoholic fermentation of the wort, it is usually heated for a few minutes at 70° to 75° to kill these germs. This procedure has, however, the disadvantage of destroying the diastase, which can always play a part during the fermentation, and of increasing the quantity of dextrin.

In the Effront process (*see later*), the fermentation is carried out in presence of hydrofluoric acid, which kills all the bacteria but not the yeast (previously acclimatised to the hydrofluoric acid), so that the saccharification may be effected at the most favourable temperature (55°) without subsequently heating to 75°.

As soon as the saccharification is terminated, the wort should be cooled to about 20°, and the fermentation started. This cooling may be accomplished in the masher, with suitable internal coolers (Fig. 110), but it is better done in appropriate apparatus.

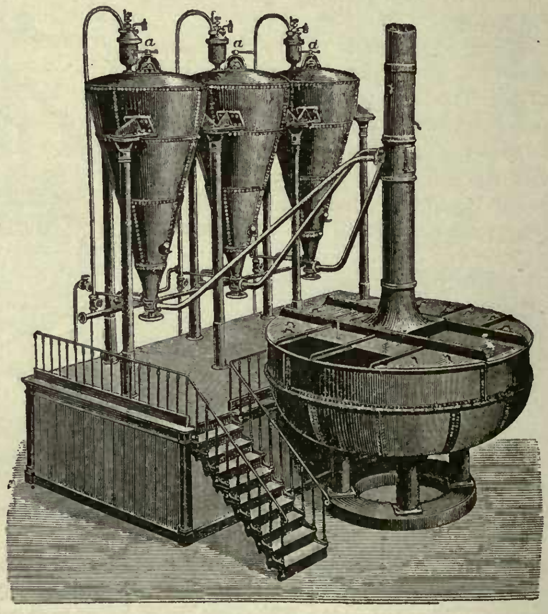

Fig. 112.

One form of horizontal Hentschel *refrigerator* is shown in Fig. 113. The horizontal rotating axis (40 to 50 turns per minute) is formed of a tube, to which is fastened a deep screw and in which cold water circulates from *h* to *k*. The screw moves in a horizontal cylinder through which the hot wort is forced by the screw in a direction (*b* to *f*) opposite to that taken by the water; the temperature of the wort at the outlet, *f*, is controlled by regulating the flow of wort and water, and, if necessary, by spraying the exterior of the cylinder with water by means of the tube *l*. With 700 c.c. of water, a litre of wort is cooled from 60° to 16°.

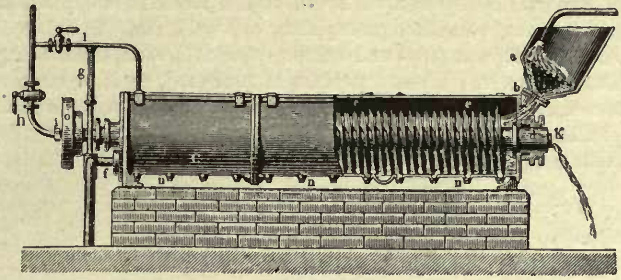

FIG. 113.

To separate the solid residue, husks, etc. (*grains*), from the wort, the latter is filtered cold through dehuskers, which have different forms, some fixed and some revolving. The most recent Pauksch type consists of a kind of centrifuge (hydro-extractor) with a fine copper gauze basket, almost like the centrifuges used in sugar factories (*see* Sugar).

Brewers and distillers often use also the Hentschel dehusker (Figs. 114 and 115), consisting simply of a rotating drum, with a spiral of metal gauze, which carries the drained grains to the middle and discharges it in cakes through doors which close automatically; the liquid flows to the bottom and passes to the fermenting vessels.

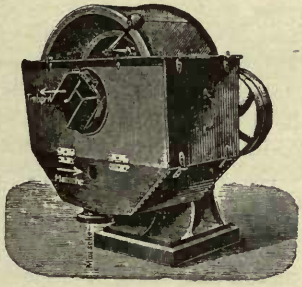

FIG. 114.

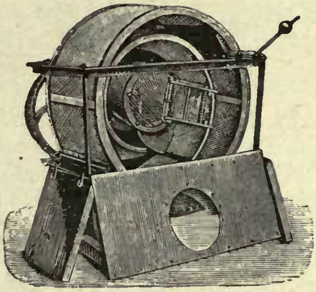

FIG. 115.

(*a*) Acetic bacteria (*b*) Lactic bacteria (*c*) Butyric bacteria

FIG. 116.

ALCOHOLIC FERMENTATION. Industrially the transformation of saccharine worts into alcoholic liquors is always effected by means of organised ferments (or yeasts). Worts left exposed to the air at 15° to 30° ferment spontaneously, but, owing to the different species of bacteria present, not only alcoholic fermentation, but also harmful secondary fermentations, such as the acetic, lactic, butyric, etc. (the corresponding bacteria are shown in Fig. 116), develop.

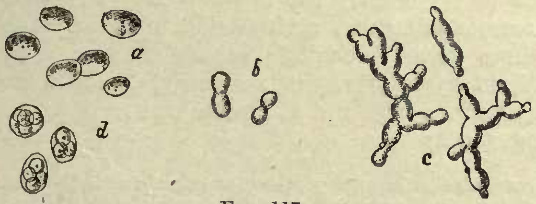

FIG. 117.

Owing to the studies of Rees, and more especially of Hansen, it is nowadays admitted by everybody that the principal agent of alcoholic fermentation is *Saccharomyces cerevisiæ* (Fig. 117, *a*, *b*, and *c*), a fungus that multiplies by budding and has varying dimensions (2·5 to 10 μ) and appearance according as it develops at the surface (Fig. 118) or in the body of the wort (Fig. 119). In Fig. 120 is represented a cell of the ferment magnified 4000 times and showing the granulations, vacuoles, protoplasm, cell-wall, etc. In spirit distilleries, a mixture of two varieties of yeast (top- and bottom-yeasts) is used, these being of the same race, but not interconvertible; often top-yeast is preferred, as it is more active, whilst in lager-beer breweries, where the fermentation is slow, bottom-yeast is mostly used (*see later:* Beer).

The final result of the decomposition of maltose by yeast may be expressed thus:

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_5 \cdot OH + 4CO_2;$$

actually, however, the maltose and dextrin formed from the starch are transformed into glucose by the action of the maltase contained in the ferment along with the zymase, the latter then converting 95 per cent. of the glucose into alcohol and carbon dioxide with development of heat (if the glucose were transformed completely into $H_2O + CO_2$, the evolution of heat would be seven times as great):

$$C_6H_{12}O_6 \text{ (glucose)} = 2C_2H_5 \cdot OH + 2CO_2 + 22{,}300 \text{ cals.}$$

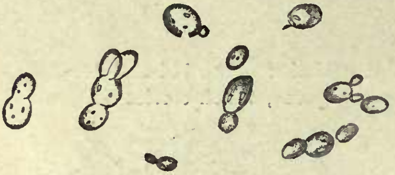
FIG. 118.

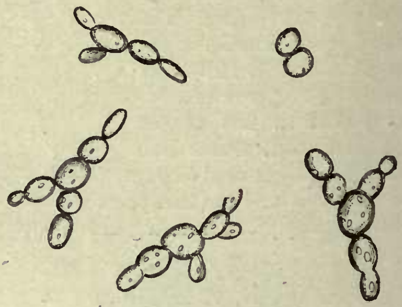
FIG. 119.

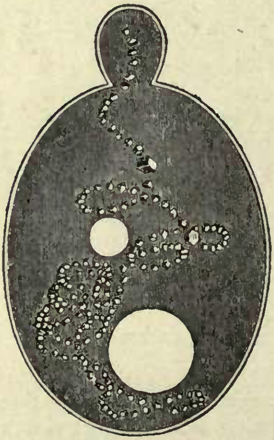
FIG. 120.

In general ferments decompose or ferment carbohydrates containing in the molecule a number of carbon atoms divisible by three, but they exhibit a preference for certain stereoisomerides.

A small part of the sugar serves for the growth and multiplication of the yeast (Pasteur), about 3 per cent. of it is converted into glycerol,[1] about 0·5 per cent. into succinic acid, and the remainder into higher alcohols forming *fusel oil*, this consisting mostly of amyl alcohol ($C_5H_{11} \cdot OH$, *isobutylcarbinol*), with small proportions of isopropyl alcohol, butyl alcohols, and esters. Ehrlich (1909) has shown, however, that fusel oil and succinic acid are formed by the decomposition of the amino-acids which constitute the cells of the ferment.

For their nutrition yeasts, like bacteria (*see* p. 132), derive carbon from the sugars (maltose, etc.), and, in some cases, even from methyl and ethyl alcohols (4 per cent.); the nitrogen may be taken from ammonium salts, amino-acids, nitrates, urea or even free ammonia. Sometimes yeasts assimilate certain sugars (*e. g.*, maltose, melibiose, raffinose) without hydrolysis being necessary, *i. e.*, without fermenting them, while sometimes various sugars (*e. g.*, glucose and saccharose) are not assimilated, but are fermented.

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[1] The formation of *glycerol* during fermentation has not yet been explained; it is thought that it forms a direct secondary product from the decomposition of the sugar into alcohol and CO_2, or that it results from the action of lipase on the fats and oils of the ferment cells; Buchner (1906) holds that it is formed from the sugar, but by a special process; Reisch (1907), however, finds no relation between the amounts of alcohol and glycerol formed, and hence regards it not as a product of fermentation, but rather as a metabolic product of the yeast.

The theoretical yields of pure alcohol from various sugars are as follow:

100 grams of saccharose	$C_{12}H_{22}O_{11}$	—51·11	grams or	64·6	c.c. of alcohol
,, ,, maltose	$C_{12}H_{22}O_{11}$	—51·11	,,	64·6	,, ,,
,, ,, starch	$(C_6H_{10}O_5)_x$	—56·80	,,	71·8	,, ,,
,, ,, glucose	$C_6H_{12}O_6$	—48·67	,,	61·6	,, ,,

Various sugars, however, do not ferment directly (saccharose, lactose, etc.), but must first be inverted, that is, transformed into *hexoses* (fermentable sugars with six carbon atoms), but ordinary alcoholic ferments (saccharomycetes) contain the inverting enzymes (besides zymase), and hence can effect inversion and then fermentation.[1]

The fermentation industries in general, and the alcohol industry in particular, have made marked progress since the introduction of pure ferments. The cultivation of pure yeasts has at the present time become a special industry of great importance; all precautions are taken to select and cultivate well-defined races of ferments, and this is especially owing to Hansen of Copenhagen, who, by thirty years of study and experiment, showed the great practical value of the selection of yeasts. The first pure culture is made in a *moist chamber* of glass, *c* (Fig. 121), fixed on a microscope slide, *d*; the whole is sterilised, either by a flame or by heating for two hours in an oven at 150°. Sterilised water is placed on the bottom of the chamber to keep the atmosphere moist, and the chamber placed in an incubator at 30° to 35°. The yeast culture is developed in a drop of gelatine, *b*, adhering to the lower side of the cover-glass covering the chamber.

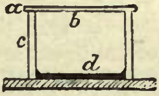

FIG. 121.

The culture of pure ferments may also be carried out in Chamberland flasks of 30 c.c. capacity (Fig. 122), half filled with nutrient gelatine and fermentable substances, and covered with a glass cap full of sterilised cotton-wool.

The more or less pure yeast which it is desired to cultivate is introduced by means of a sterile platinum wire into a flask containing sterile water, which is well mixed and should become just turbid. A drop of this water is then examined under the microscope in order to ascertain the number of yeast cells it contains. By means of a platinum wire sterilised in a flame, a drop of the water is introduced into a Chamberland flask containing liquefied gelatine at 35°. After the latter has been well shaken, a drop of the gelatine is examined microscopically on a glass micrometer (marked with crossed lines) to see that there are not too many or too few cells present, since the colonies that ultimately develop from the single cells should remain sufficiently far apart from one another not to mingle. Of this inoculated gelatine, one or more drops are placed on the cover-glass of the moist chamber, this being kept under a bell-jar until the gelatine has solidified and then placed, upside down, on the chamber. In a thermostat at 25° the yeasts are usually sufficiently developed after two or three days, and the various colonies are then examined under the microscope to ascertain if one or more of them are pure, that is, constituted of similar cells of one and the same yeast. Each of the pure colonies is touched separately with a small piece of sterilised platinum wire, which is immediately dropped into a Pasteur flask (125 c.c.) charged to the extent of two-thirds with a nutritive solution (*e.g.*, malt wort) (Fig. 123), the rubber tube being momentarily removed. The flask is at once closed again, and is then kept in a thermostat at 25° to 28°. After two days the liquid will be in a state of active fermentation, a large quantity of the yeast having been formed. Each of these flasks represents a pure culture (provided that the proper precautions have been taken in

FIG. 122.

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[1] According to Boysen-Jensen (1909) the *zymase* of alcoholic ferments is constituted of two enzymes: *dextrase* and *dihydroxyacetonase*, glucose first forming 2 mols. of *dihydroxyacetone* $OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH$ (*triose, see* p. 136), which to a small extent may be fixed in the form of oxime or hydrazone (*which see*) by means of hydroxylamine hydrochloride or methylphenylhydrazine acetate; the dihydroxyacetonase then decomposing the dihydroxyacetone into $2CO_2$ and $2C_2H_5OH$. The dextrase alone would give directly alcohol and CO_2 if glycerol were added to the solution of glucose. With zymase (which contains dihydroxyacetonase), pure dihydroxyacetone gives alcohol and CO_2, whilst with oxydases it gives only CO_2.

the inoculation). All the cultures are, however, examined, one or two drops from each flask being observed under the microscope.

These pure yeasts or other pure ferments are largely used by brewers and distillers, who have yeasts suited to their needs selected and preserved by scientific institutions, from which cultures in Pasteur flasks are despatched to them when the organisms in their own fermenting vessels begin to degenerate or become contaminated. In Fig. 124 is shown diagrammatically an apparatus for the industrial preparation of selected yeast; the metal reservoir, *C*, provided with a safety-valve, *q*, and a manometer, *r*, is filled, by means of the pump, *u*, with air filtered through a cotton-wool filter, *t*, and compressed under a pressure of 3 to 4 atmos. The vessel, *A*, is first sterilised with steam under pressure, which enters at the tap, *f*, whilst the air is driven out through the tube *b*, dipping into a vessel of mercury forming a seal. When the cock, *f*, is shut, *g* is opened so as to allow air to filter through *d* into *A*. Hot wort is introduced into the reservoir, *A*, heated to boiling and then cooled by means of a water-spray issuing from an annular tube, *e*, and bathing the outside of *A*. The fermenting vessel, *B*, which is sterilised in the same way as *A*, is also furnished with a cotton-wool filter, *h*, and a hydraulically sealed tube, *i p*, through which the CO_2 is to escape; the glass tube, *O*, which is a continuation of the filter, indicates the level of the liquid inside the vessel. It is further provided with a vertical stirrer which is set in motion by the handle, *k*, and serves to mix the wort and yeast which are introduced through the small tap, *l*. A slight air-pressure is maintained in both *A* and *B* in order to prevent external contaminated air from entering either when the discharge-cock, *m*, for the fermented wort is opened or through any leaks there may be in the apparatus. In this way *B* may be used for a year or more without contamination taking place, a little residual yeast being left after each operation to ferment the succeeding charge of wort. The sterile wort, cooled to 15°, is passed from *A* into *B* by means of the tube *a n*, and before it reaches the level of the tap, *l*, the pure yeast contained in a Pasteur flask is introduced through this tap; *B* is filled to the extent of about three-fourths (about 200 litres) with the wort from *A*, the whole being then well mixed. When the fermentation is ended (in three or four days with worts for alcohol production, or in eight to ten days for beer worts), the yeast is allowed to settle; the fermented wort is discharged from *m* by increasing the pressure of the air and, when it begins to issue turbid (owing to suspended yeast), *m* is closed and about 30 litres of wort introduced from *A* and well mixed in, 30 litres of the turbid yeasty liquid being then run off from *B*, this amount being sufficient to induce fermentation in 40 hectolitres of wort in the ordinary fermenting vessels; a further quantity of 30 litres of wort is then run in from *A* and, after mixing, another 30 litres of yeasty wort drawn off. That remaining in *B* serves for the next operation. This is the procedure adopted in large breweries and distilleries, whilst in yeast-factories the wort is prepared from barley and rye under the action of malt for an hour at 60° and for about twenty-four hours at 40° to 44°, in order to produce about 1 per cent. of lactic acid, which peptonises the proteins and so affords better nutriment for the yeast, the action being completed by

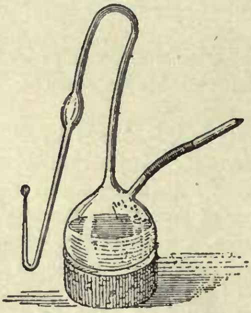

FIG. 123.

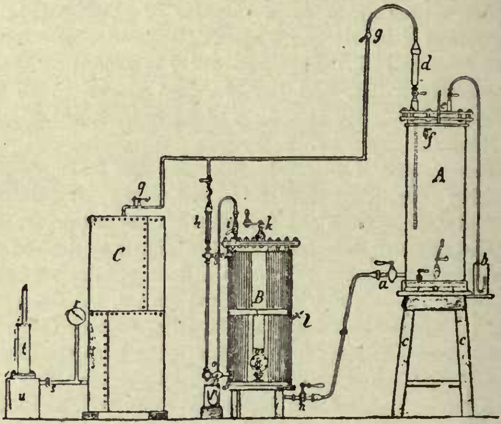

FIG. 124.

the addition of 10 grams of sodium or ammonium phosphate per hectolitre of wort. The wort is then fermented as above at 18° to 20°, and the yeast, which is formed in large quantity, is washed with water by decantation, freed from excess of water in centrifuges or filter-presses, and made into a paste with 5 to 10 per cent. of potato-starch, forming cakes which are sold under the name of *pressed yeast.* 100 kilos of rye yield 16 kilos of yeast.[1]

[1] **Yeast Industry.** In Germany more than 21,000 tons of yeast were made in 1910, from 1000 to 1300 tons being exported annually; in five factories alone over 11,000 tons were produced in 1909. In 1912 the output reached 43,000 tons.

Italy imported the following quantities of yeast:

	1905	1908	1910	1912	1913	1914	1915	1916
Tons . . .	136	292	362	582	569	210	30	9·7
Value (£) . .	—	—	18,080	20,940	20,495	7,564	1,080	—

Certain of the French factories export as much as three or four tons of pressed yeast per day. In Austria, the law of May 18, 1910, regulates the trade in yeast so as to prevent adulteration and mixture.

In October 1912, the syndicate of German yeast manufacturers decided to lower the price by twopence per kilo (to about 10*d*. per kilo), owing to the lower prices of the raw materials (barley, rye, etc.) in the world's markets, and with the view of preventing development of the works outside the syndicate. Formerly the addition of 20 per cent. of starch to the yeast was allowed (if declared), but such addition is now prohibited.

Yeast is used (after repeated washing to remove bitter substances, and subsequent drying) as a concentrated food for invalids (*marmite*) and as concentrated fodder for cattle (removal of the bitter matter then unnecessary). With hens and geese it has given results as good as those obtained with meat powder (in increasing the output of eggs). As human food it serves to replace plasmon and somatose (as it contains 2 per cent. of lecithin); it is used also in the treatment of boils, etc. Its nutritive properties are due to its highly assimilable protein substances, these in somatose costing more than £4 per kilo. In the moist state it contains 75 to 80 per cent. of water, but with care it may be dried without loss in nutrient quality; a sample of such dried yeast showed on analysis the percentage composition: water, 1·5 to 3; ash, 8; crude protein, 54; cellulose, 1·5; non-nitrogenous extractives, 29; lecithin, 2·2. To obtain dry yeast, the yeast may be suspended in water and air passed through the latter for seventy-two hours, the protein matters being thus modified so that they withstand gradual drying; another process consists in mixing sugar with the pressed yeast and drying at 50°.

In Germany until 1912 there was a large excess of yeast not utilised. If the waste yeast from all the fermentation industries were collected, it would amount to about 70,000 tons per annum (in Germany). If, however, all the pressed yeast were used as concentrated fodder, the output would be insufficient. The yeast distillery of Delft (Holland) produced more than 7500 tons of yeast and 200,000 hectolitres of alcohol in 1912. The largest consumers of pressed yeast are the bakers.

At one time, with a yield of 30 to 32 per cent. of alcohol on the weight of cereal used, the amount of yeast obtained was 12 to 14 per cent. During recent years a marked increase has been effected in the quantity of yeast (up to 20 per cent.), the yield of alcohol being diminished by vigorous aeration of the wort during fermentation (30 to 40 cu. metres of air per hour for every 100 kilos of cereals converted into wort). By the new *Braasch process* the yield of yeast may be raised to 40 per cent. and that of alcohol lowered to 15 per cent. (under some conditions of the market the production of yeast is more remunerative than that of alcohol). The value of yeast in Germany is calculated at about £38 to £40 per ton, and some factories produce as much as 500 to 1000 tons per annum; the alcohol is valued at £1 8*s*. per hectolitre.

In the old Vienna process, worts of 10° to 20° Balling (or even heavier) were fermented by means of yeasts prepared with worts rich in lactic acid (100 c.c. of this wort should require 12 to 14 c.c. of normal sodium hydroxide solution for neutralisation). When the fermentation was complete, the yeast was collected by means of ladles and despatched along channels into vats, where its activity was arrested with cold water. After this, it was shaken on silk sieves, which retained all the husks or grains; the yeast passing through the sieves was washed two or three times with water and, after settling, pressed into cakes. In 1887–1890 all yeast factories worked on this plan, but nowadays only few of them do so.

The new Braasch aeration process starts from clear wort and green malt (non-kilned). The cereals for preparing the mash and thus the wort are no longer ground, but are softened with water and then crushed. The mashing of the green malt is carried out in a medium slightly acidified with sulphuric acid, the lactic ferment (*Bacillus Delbruckii*) being allowed to act, after the diastase, for several hours at 40° to 50°. When the desired acidity is reached, further acidification is prevented by heating the whole mass to 68° to 70° (the total amount of sulphuric and lactic acids, without CO_2, corresponds with 5 c.c. of normal NaOH per 100 c.c. of wort). The concentration of the wort used was at one time 12° to 14° Balling, but at the present time 10° Balling is preferred. The temperature of fermentation is about 25°. If the acidity of the wort is less than 2 c.c. of normal soda per 100 c.c., the yeast obtained is flocculent and separates badly. The separation of the yeast is now effected thoroughly and rapidly in centrifuges. The fermentation is started by adding to the wort 4 to 5 per cent. of yeast (calculated on the weight

In France, and latterly in Italy, industrial spirit distillers are making use of the Jacquemin apparatus (Fig. 125) for the preparation of pure yeast cultures. The peptonised wort is prepared as described above, and the sterilised air, compressed by the pump *A*, passes through a filter of cotton wool moistened with mercuric chloride, *F*, into a battery of vessels, *G*, the first and third of which are empty, whilst *S* contains sulphuric acid and *n* soda solution; the empty vessels serve as safeguards, in case the liquids are sucked backwards. The air sterilised in this way passes along suitable pipes to all the fermenting vessels, *B*, *B′*, *C*, *C′*, *D*. *B* is two-thirds filled with the peptonised wort (20 to 30 litres), which is boiled for a few minutes by steam entering through *b* and then cooled by passing a vigorous current of air through the wort and by an annular spray of water applied to the outside of the vessel *B* by the tube *e*. When the temperature has fallen to 20°, the contents of a Pasteur flask of pure yeast are introduced through the tube *a*, and the fermentation allowed to proceed for twenty-four hours; in the meantime, wort sterilised and cooled to 20° is prepared in *B′*; a little of the yeast is then passed from *B* through the tube *t* to *B′*, the remainder being discharged, by the three-way cock, *t*, into the larger vessel, *C*, which contains sterilised wort (250 to 300 litres). When the fermentation has reached an advanced stage (a definite *attenuation: see later*), the wort is discharged through the tube *r* into *D*, which also contains sterilised wort, and that remaining on the bottom of *C* is forced by compressed air into the vessel *C′*, previously charged with sterile wort.

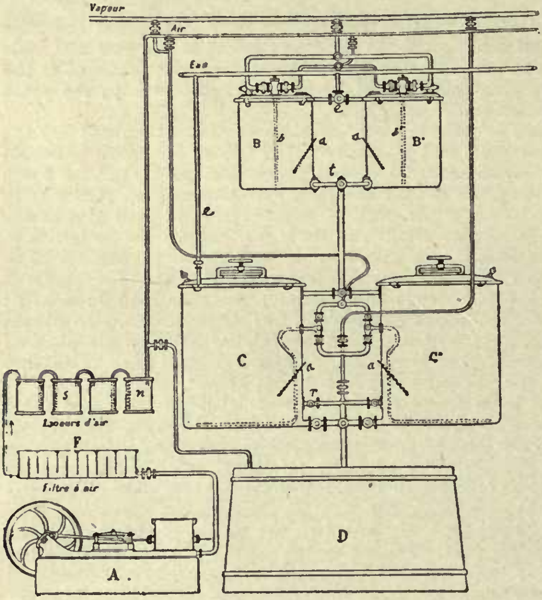

FIG. 125.

It will be seen that, by this procedure, the working is continuous, and the yeast is renewed only once or twice per month. The yeast may then be separated from *D* and pressed, or the actively fermenting wort (5 to 6 hectolitres) may be used to induce fermentation in the factory vats containing ordinary wort.

The selected yeasts are controlled practically, by measuring their fermentative activity and by determining the concentration with the microscope and cell-counters, note being taken of extraneous organisms.

Pressed yeast in cakes keeps for several days if well wrapped in paper and placed in tightly closed boxes in a cool room; otherwise it soon becomes covered with mould and unusable. When the stock of yeast is larger than is required, it may be dried at a cost of 10*s*. per ton and sold as a good cattle food. To prevent secondary fermentations from taking place, instead of the lactic acid fermentation, during the preparation of selected yeasts, Bücheler (Ger. Pat. 123,437) suggests the addition of 180 c.c. of concentrated

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of cereals used) and is finished in ten to twelve hours; the yield of 40 per cent. (on the weight of cereals) of yeast is in addition to the amount added (5 per cent.). The yeast cultures should be renewed occasionally.

The fermented wort is feebly alcoholic (less than 1 per cent. of alcohol), so that the distillation and rectification necessary to obtain 90 to 95 per cent. alcohol are very expensive; further, the alcohol is not of good quality and is hence only suitable for denaturing. The diminished yield of alcohol is due partly to loss of the alcohol carried away by the large volumes of air passed through the wort, and partly to destruction of maltose by ferments or enzymes developing in presence of excess of air. The less the amount of air used, the greater is the amount of spirit obtained.

In the control of the purity of the yeast, account must be taken of the extraneous ferments, of the quantity of starchy substances (when starch is not added this does not reach 4 per cent.), and of the fermentative activity.

sulphuric acid to every hectolitre of wort; the process yields excellent results in practice, notwithstanding the disputing of the patent from 1900 to 1909, owing to the fact that a similar patent (No. 3885) was granted in Austria to Bauer in 1900.

FACTORS WHICH FACILITATE OR RETARD FERMENTATION. Alcoholic fermentation may be hindered by various factors. Very concentrated sugar solutions do not ferment, whilst with a concentration of 70 per cent., only 6 per cent. of the sugar is converted into alcohol; with a strength of 60 per cent., 25 per cent. is transformed, and when the concentration is 30 per cent. it is possible, although not without difficulty, to convert 92 per cent. of the sugar into alcohol.

Temperature has also a very marked influence on alcoholic fermentation, which at 0° or at 60° ceases completely; later we shall see at what temperature the process takes place most regularly from the point of view of the industrial yield.

Alcohol, although a product of fermentation, when it reaches a certain concentration, may prevent further fermentation. This anti-fermentative action of the alcohols is, to some extent, proportional to their molecular weights. Thus the fermentation of glucose may be arrested by 20 per cent. of methyl alcohol, 16 per cent. of ethyl alcohol, 10 per cent. of propyl alcohol, 2·5 per cent. of butyl alcohol, 1 per cent. of amyl alcohol, and 0·1 per cent. of capryl alcohol.

ANTISEPTICS, in general, prevent fermentation when they are present in relatively high concentrations; they may, if their dilution is great, exert a favourable influence on fermentation.[1]

However, since the favourable action exhibited by these solutions depends on the quantity of yeast present and that of the antiseptic dissolved, it is possible, when the quantity of yeast is large, that solutions more concentrated than those indicated in column (B) may produce favourable effects on the fermentation. It is unnecessary to state that these concentrations vary somewhat with the nature of the organisms. It has been shown recently (1910), for example, that *Staphylococcus pyogenes aureus* resists a 2·7 per cent. solution of mercuric chloride for six hours.

The organic acids also exert an unfavourable influence on alcoholic fermentation,[2] whilst, within certain limits, lactic and formic acids and formaldehyde have a beneficial action, since they prevent the development of harmful bacteria and are readily tolerated by alcoholic ferments specially *acclimatised* to their action. By adding small quantities of formaldehyde and of sterilised milk (which then gives lactic acid), the yield of alcohol has recently been increased by as much as 2 per cent. E. Soncini (1910) has shown that the course of fermentation in general is closely connected with the chemical medium in which it takes place; thus, in a saccharine wort (from bananas), the lactic fermentation first develops spontaneously and proceeds until the lactic acidity reaches a certain limiting amount; this may be followed by alcoholic fermentation, which, in its turn, may be succeeded by the acetic fermentation; the lactic fermentation may ultimately begin again. It is only by considering all these conditions that a regular alcoholic fermentation and a good yield of pure alcohol may be assured, since in general the secondary

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[1] Thus, for example :

	(A) *The most dilute solution capable of preventing fermentation is:*	(B) *The most concentrated solution capable of favouring fermentation is:*
Mercuric chloride	1 in 20,000	1 in 300,000
Potassium permanganate .	,, 10,000	,, 100,000
Bromine	,, 4,000	,, 50,000
Thymol	,, 3,000	,, 20,000
Salicylic acid . . .	,, 1,000	,, 6,000
Phenol	,, 200	,, 1,000
Sulphuric acid . . .	,, 100	,, 10,000
Boric acid	,, 25	,, 8,000

[2] The action of some of the commoner acids is as follows :

	Dose that retards alcoholic fermentation	Dose that arrests alcoholic fermentation
Acetic acid	0·50%	1·0%
Formic ,, ...	0·20%	0·30%
Propionic acid . . .	0·15%	0·30%
Valeric ,, . . .	0·10%	0·15%
Butyric ,, . . .	0·05%	0·10%
Caproic ,, . . .	—	0·05%

and harmful products of the fermentation (higher alcohols, such as amyl, etc.) result from the actions of extraneous micro-organisms. The carbon dioxide formed during fermentation may give rise to pressures as high as 12 atmos. if hermetically sealed vessels are used, and the action of the yeast is then retarded or even arrested.

PRACTICE OF FERMENTATION. To start the fermentation of the worts prepared as described above, various methods are used: in some cases a portion of old, fermented wort from a preceding operation is employed, but this is not a rational method, because the yeast in the old wort is in a condition unfavourable to development and is also contaminated with other micro-organisms which would develop readily in the new wort. To be preferred is the custom followed by certain distilleries of starting the fermentation with brewery yeast, which is cheap and comparatively pure. The best and most rational method is, however, the use of selected yeast in culture wort or in a pressed condition (*see above*), as supplied by various firms and institutions which guarantee its purity. By this means alone it has been possible during the past few years to increase the mean yield of alcohol in distilleries by 0·5 per cent. or even 1 per cent., and at the same time to improve the quality of the product.

It is advisable to ferment worts as soon as they are prepared and cooled to 15° to 20°, delay resulting in contamination with heterogeneous germs always present in the air.

To avoid secondary fermentations as far as is possible, addition is often made to the wort of antiseptics, to which the selected yeasts have been habituated. Thus, small proportions of calcium bisulphite or, better, of ammonium or aluminium fluoride are added, the hydrofluoric acid—liberated under the action of the acids formed in the secondary fermentations—killing the harmful organisms. With the Effront process, hydrofluoric acid (*see* Vol. I., p. 167) is added directly in the proportion of 5 or even 10 grams per hectolitre of wort (some yeasts resist as much as 100 grams of HF per hectolitre). Sometimes a selected lactic ferment (*Bacillus acidificans longissimus*) is added, this also favouring the production of pure alcohol.

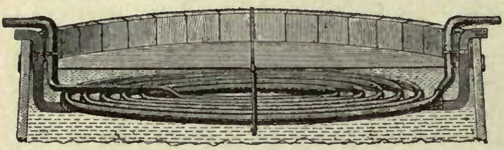

FIG. 126.

The use of these yeasts acclimatised to the action of hydrofluoric acid renders possible the employment of the temperature 55° to 57° (*see above*) for the previous saccharification of the starch by diastase, this low temperature resulting in the formation of an increased amount of maltose; also if there are other noxious living micro-organisms in the wort, these are killed by the hydrofluoric acid during the fermentation.

Effront, however, succeeded in preparing yeasts capable of fermenting with ease also the dextrin; when these are used, the saccharification with diastase may be effected with less malt and at 64° to 65°, so that harmful micro-organisms are killed. All the apparatus, instruments, and vats which come into contact with the wort should be previously washed with dilute hydrofluoric acid solution (100 grams per 25 litres of water).

For every hectolitre of wort are added about 30 grams of pressed yeast in small quantities mixed with increasing quantities of wort and well stirred in; the fermentation then starts immediately.

The fermentation of the wort proceeds in three successive phases:

(1) *Preliminary fermentation*, in which the yeast develops and grows, the most favourable temperature being 17° to 21°.

(2) *Principal fermentation*, in which the maltose and glucose are fermented, best at 26° to 30°.

(3) *Secondary fermentation*, in which the dextrins are fermented, the diastase continuing to saccharify the remaining dextrins as the wort becomes warm, the best temperature being 25° to 27°.

The vats, holding 10 to 90 hectolitres, and often furnished with stirrers, are filled with wort to the extent of nine-tenths. The temperature is regulated by suitable cold-water coils (attemperators, Fig. 126), which are of various forms (*see* Beer). In general, these attemperators have a surface of 0·3 to 0·4 sq. metre per 10 hectolitres of wort. Fermentation is begun in the vats at 12° to 15°, and after two or three hours the temperature rises and the fermentation becomes vigorous. The liquid is then agitated to liberate the CO_2, thus diminishing the pressure in the mass and facilitating the fermentation, the temperature not being allowed to exceed 28° to 29°. After two days, the principal fermentation ceases and the temperature is maintained at 25° to 26° for a day, the fermentation being thus completed.

Worts that are too dilute or are made from poor malt or impure grain give a boiling fermentation that hurls the liquid from the vat and renders the subsequent distillation difficult. This inconvenience is avoided by using more concentrated worts and good yeast, or, in case of necessity, adding 100 to 200 c.c. of oil to each vat.

Ammonium fluoride (2 to 25 grams per hectolitre) or hydrofluoric acid (rather less) is often added to the wort before fermentation.

In some modern distilleries covered fermenting vats or wash backs are used, these giving good results also in beer brewing (*q. v.*). By this means the CO_2 may be utilised, while the yield of alcohol is increased by 2 to 3 per cent., that carried away by the CO_2 being recovered from the wash liquors of the gas.

LOSSES AND YIELDS. A residue of unfermented starch (0·7 to 2 per cent.) and dextrin (5 to 8 per cent.) always remains after fermentation. In every fermentation 2 to 3 per cent. of glycerol is formed; also part of the sugar serves as food for the yeast and part of the alcohol evaporates, this making a total loss of 6 to 8 per cent.

Starting with 100 parts of starch, 12 to 20 parts are usually lost in various ways, while with improper working the loss may reach 28 per cent.

If the starch could be transformed *theoretically* into alcohol and carbon dioxide alone, 100 kilos of starch should yield 71·6 litres of pure alcohol; allowing for these losses and working under the best conditions, 63·5 litres of alcohol are obtained; 60 litres is a good yield and 58 litres a medium one, whilst 55 litres would indicate bad conditions of working. The mean starch-contents of many of the prime materials used in the distillery are given on p. 141; that of green malt (from good barley) is 38 to 42 per cent., and that of kilned malt, 65 to 70 per cent. Whilst in 1883 Italian distilleries gave an average yield of 315 litres of alcohol per ton of maize, in the season of 1904–1905 the yield (official statistics) amounted to 340 litres, and now about 355 litres is obtained.[1]

For calculating the yield, the exact analyses of the prime materials, starch and sugar, must be known. The sugar-content of a wort is determined from the density by means of the Balling *saccharometer* modified by Brix, *degrees* Brix (or Balling) read at 20° (formerly 17·5°) indicating directly the percentage of sugar in the solution. In worts, however, part of this density is due to unfermentable substances.

As fermentation proceeds, the proportion of alcohol increases and the density diminishes; this diminution is called the *degree of fermentation* or *attenuation*. The density is measured before, during, and after the fermentation on the filtered wort, and if it filters badly it is diluted with a *definite* volume of water.[2] When the fermentation

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[1] From 90 kilos of maize and 10 kilos of malt, 36 litres of pure alcohol may be obtained, and from 100 kilos of potatoes (with 18 per cent. of starch) and 1·8 kilos of malt, 12 litres. If the maize costs £8 per ton (1000 kilos) and the potatoes £2 4*s*., it is advantageous to use maize, in spite of the fact that 120 kilos of coal are consumed per 100 litres of alcohol from potatoes and 150 kilos in the case of maize. The maize residues (grains) are worth almost three times (about 13*s*. per hectolitre of alcohol) as much as the corresponding quantity from potatoes. The cost of labour, lubricants, antiseptics, etc., was estimated in Germany before the War to be 2*s*. per hectolitre of alcohol.

[2] The density, p, before fermentation is due to x parts of sugars $+$ z parts of non-fermentable substances; if the density after fermentation indicates the magnitude, z, then $p - z = x$. This does not give the absolute attenuation, since z is altered by the presence of alcohol and carbon dioxide. If the carbon dioxide is eliminated by shaking and gentle heating, a density, m, is obtained and the magnitude of $(p-m)$ gives the so-called *apparent attenuation* (apparent because alcohol is still present); the amount of alcohol formed may be allowed for by means of a known factor, a, the *real attenuation* being given by $A = a(p-m)$. The value of a is determined by distilling a small quantity of fermenting wort, and calculating the value of the expression $a = \frac{A}{(p-m)}$; a is, however, not a constant, but varies with the nature of the sugars, with the original concentration, p, and with the stage of the fermentation (incipient, vigorous, or secondary). If a is known, the quantity of alcohol obtainable from a *fermented* wort of a given density may be calculated.

The ratio between the *apparent attenuation* $(p-m)$ and the original saccharometer reading, p, gives the so-called *degree of apparent fermentation* (B). If $p = 25°$ and the density (m) of is finished and the degree of attenuation controlled, the resultant fermented wash (with about 9 to 11 per cent. of alcohol) is subjected to distillation and rectification in order to

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the fermented wort is 3, we have $B = \frac{25 - 3}{25} = 0{\cdot}880$, which is the *degree of apparent fermentation*, and indicates that, of every unit of saccharine substances, 0·880 part have disappeared, *i. e.*, have been fermented. From the degree of apparent fermentation (B), the degree of apparent attenuation may, of course, be obtained: thus, $\frac{p—m}{p} = B$ gives $p—m = Bp$; and from the factor a mentioned above, the amount of alcohol resulting from such degree of apparent fermentation is known.

The *real attenuation* (A') is determined by distilling a certain quantity of the fermented wort until its volume is reduced to one-third, the residue being made up to the original volume with water and the density, n, measured; the real attenuation then $= p—n$. Since, however, the residue always contains unfermented matter, in order to calculate the alcohol, a factor, b, is determined in the same way as the factor a, *i. e.*, by distillation of a part of the fermented wort; the quantity of alcohol can then always be determined from the density of the fermented wort, for, since $A' = (p—n)\,b$, $b = \frac{A'}{p—n}$. Similarly, the *degree of real fermentation* will be $B' = \frac{(p—n)}{p}$, which expresses the fraction of the extract (dissolved substance without alcohol) really fermented, the manufacturer being thereby able to judge if the fermentation proceeds normally and to establish comparisons with previous fermentations, etc.

The apparent attenuation (alcohol being present) is always greater than the real (derived after elimination of the alcohol), and the *attenuation difference*, D, is obtained by subtracting one from the other, $(p—m)—(p—n) = D$. This magnitude, D, is therefore equal to $n—m$ and increases as the fermentation proceeds towards completion; also here the quantity of alcohol already formed is found by determining experimentally a factor, c, in the usual way, so that $\frac{A}{n—m} = c$, or $A = (n—m)c$. The ratio of the apparent to the real attenuation, $\frac{p—m}{p—n} = q$, gives a *quotient of attenuation* which varies with the concentration of the liquid but becomes constant towards the end of the fermentation and shows how much the apparent fermentation is greater than the real; by its means, almost all the saccharometric calculations may be made: $\frac{b}{q}$ = the alcohol factor for the real attenuation, and if this is divided by q diminished by unity

TABLE FOR CALCULATING THE ATTENUATION IN FERMENTED WORTS

Saccharometer degrees of the wort	Alcohol factors for the attenuation		Factors for the attenuation differences	Attenuation quotient	Values of $\frac{c}{b}$
	Apparent	Real			
p	a	b	c	q	
6 . . .	0·4073	0·4993	2·2095	1·226	4·4247
7 . . .	0·4091	0·5020	2·2116	1·227	4·4052
8 . . .	0·4110	0·5047	2·2137	1·228	4·3859
9 . . .	0·4129	0·5074	2·2160	1·229	4·3668
10 . . .	0·4148	0·5102	2·2184	1·230	4·3478
11 . . .	0·4167	0·5130	2·2209	1·231	4·3289
12 . . .	0·4187	0·5158	2·2234	1·232	4·3103
13 . . .	0·4206	0·5187	2·2262	1·233	4·2918
14 . . .	0·4226	0·5215	2·2290	1·234	4·2734
15 . . .	0·4246	0·5245	2·2319	1·235	4·2553
16 . . .	0·4267	0·5274	2·2350	1·236	4·2372
17 . . .	0·4288	0·5304	2·2381	1·237	4·2194
18 . . .	0·4309	0·5334	2·2414	1·238	4·2016
19 . . .	0·4330	0·5365	2·2448	1·239	4·1840
20 . . .	0·4351	0·5396	2·2483	1·240	4·1660
21 . . .	0·4373	0·5427	2·2519	1·241	4·1493
22 . . .	0·4395	0·5458	2·2557	1·242	4·1322
23 . . .	0·4417	0·5490	2·2595	1·243	4·1152
24 . . .	0·4439	0·5523	2·2636	1·244	4·0983
25 . . .	0·4462	0·5555	2·2677	1·245	4·0816
26 . . .	0·4485	0·5589	2·2719	1·246	4·0650
27 . . .	0·4508	0·5622	2·2763	1·247	4·0485
28 . . .	0·4532	0·5636	2·2808	1·248	4·0322
29 . . .	0·4556	0·5690	2·2854	1·249	4·0160
30 . . .	0·4580	0·5725	2·2902	1·250	4·0000

extract the alcohol and separate it from the water, yeast, and other solid and liquid substances. Before the distillation apparatus is described, certain special saccharification and fermentation processes, which have been recently applied practically, will be considered.

The AMYLO PROCESS (Collette or Boidin Process). This process is based on investigations of Calmette, Collette, Boidin, and others, who found that certain *Mucors* (moulds, *see* p. 133), isolated from impure Chinese and Japanese ferments, are capable of performing the functions of both diastase and zymase, that is, of transforming starch into alcohol by way of maltose and dextrin. Of these moulds, *Amylomyces Rouxii*, discovered by Calmette in 1892, and the *Mucors B* and *C* discovered by Collette, Boidin, and Mousain, are of most importance industrially.[1] Of the first two, the forms observed under the microscope in different stages of development are shown in Fig. 127 (*A*, *B*, *C*, *D*, and *E*).

Collette and Boidin patented in 1897 (Eng. Pat. 19,858) a process for the industrial utilisation of *Amylomyces Rouxii* for manufacturing alcohol directly from the starch of

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[*i. e.*, by $(q—1)$], the factor, c, for the difference of attenuation is obtained. The factor, c, is used for the analysis of liquids for which the value of p is unknown; also $\frac{B}{q} = B'$ (*degree of real fermentation*).

The following illustrates a practical calculation: the original saccharometric degree of a wort was $p = 16·2$, that after fermentation $m = 1$, and that after boiling $n = 3·9$; applying any one of the three factors (a, b, and c) given in the appended Table, the *apparent attenuation* becomes $A = (p—m)\ a$ (where $p = 16·2$, $a = 0·4267$) = 6·4858 per cent. of alcohol. Calculating according to the *real attenuation*, $A = (p—n)\ b$ (where $p = 16·2$, $n = 3·9$, and $b = 0·5274$) = 6·4870 per cent. of alcohol. Lastly, calculating from the *attenuation difference*, D, $A = (n—m)\ c$ (where $c = 2·2350$) = 6·4815 per cent. Hence the fermented wash consists of 6·48 per cent. of alcohol, 3·9 per cent. of unfermented extract (n), and 89·62 per cent. of water.

B. Wagner, F. Schultze, and J. Rüb (1908) suggest the Zeiss immersion refractometer as a means of determining the *attenuation:* exact results are obtained rapidly and with a small quantity of liquid (20 to 30 c.c.). A little of the wort is well shaken to get rid of carbon dioxide, and filtered through a covered filter, 5 c.c. of the filtrate being used to determine the refractometer reading, A, at a temperature of 17·5°; a further 20 c.c. is evaporated to one-half the volume in a porcelain dish to expel the alcohol, the volume being then made up exactly to 20 c.c. with water and the refractometer reading, B, taken. To the difference, $A - B = C$, 15 (the refractometer reading for water) is added, giving E; the corresponding alcohol degree (by volume), V, is then found in the following Table, and may be subsequently corrected for the density of the wort:

E:	16·2	17·5	18·8	20·1	21·4	22·8	24·2	25·6	27·1	28·6	30·1	31·7	33·3	34·9	36·4	38·0
V:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

[1] Among the *Hyphomycetes* (moulds, p. 133)—in the *Mucor* and *Mucedinæ*—Pasteur found certain varieties (*Mucor racemosus*) capable of transforming sugar into alcohol and carbon dioxide when they live immersed in the liquid out of contact of air (like the yeasts); in presence of air, they convert the sugar directly into water and carbon dioxide. These are called *facultative anaerobic* organisms. In 1887 Gayon studied other varieties which behave similarly (*Mucor alternans*, *spinosus*, and *circinelloides*), and Prinsen Geerligs investigated *Chlamydomucor oryzæ*, which is used in Java to ferment molasses. In 1892 Calmette imported from China, studied, and named *Amylomyces Rouxii*, the *Mucor* isolated from the rice-ferment used by the Chinese (which is more active than the Japanese *koji*) for the preparation of spirit; later he found this *Mucor* in rice-husks. At Tokyo in 1894, Takamine studied, and applied practically to the saccharification of rice, *Aspergillus oryzæ* (separated from Japanese *koji*, which is a mixture of yeasts and moulds used in Japan for producing alcoholic fermentation), but it did not meet with success, owing to its action being too energetic. Boidin, Collette, and Mousain investigated *Mucor β*, which is another *Mucor* separated from Japanese koji and is different from, and more important industrially than, that of Takamine; *Mucor γ*, which was separated at the same time from Tonkin rice, is of still greater practical value than *Mucor β*.

These moulds have the special property of saccharifying starch and of fermenting the sugar thus formed. Their saccharifying and fermentative activity is, however, influenced by the acids that they produce. Thus, *Amylomyces Rouxii*, which was the first to be used in practice in 1898, was abandoned later, as it transforms rather too much sugar into carbon dioxide and water and, owing to the production of 1·45 grams of acid per litre of wort (at 16° Balling), complete attenuation is obtained only in very dilute worts (7° to 8° Balling, these giving 4 to 4·5 per cent. alcohol); *Mucor β*, on the other hand, forms only 0·75 gram of acid, and can ferment worts at 10° to 17° Balling (which give 8 to 9 per cent. of alcohol) without oxidising completely more than a very small proportion of sugar.

Calmette studied more particularly the saccharifying properties of *Amylomyces Rouxii*, but in 1897 Boidin and Rolants, and simultaneously Sanguinetti (Institut Pasteur), found that this mould is also capable of transforming sugar and dextrin into alcohol; it was found later that *Mucor racemosus*, which had been already studied by Pasteur, behaved similarly. In 1895 Professor Saito, of Tokyo, isolated *Rhizopus oligosporus*, which acts like *Amylomyces Rouxii*. Good practical results are obtained also with pure cultures of Mucor Delemar.

cereals, etc., and later they utilised *Mucor* β. At the present time this process is employed on an enormous scale in various distilleries in France, Belgium, and Italy (at Savona).

As it is necessary to work with perfectly aseptic worts, the starch-paste prepared in the ordinary way with the Henze apparatus is passed into closed metal cylinders holding 200 to 1000 hectolitres, and furnished with vertical stirrers. When the temperature reaches 65°, 1 per cent. of malt (on the amount of maize used) is added to render the mass rather more liquid; after an hour the mash is slightly acidified by the addition of 0·1 gram of sulphuric acid per litre, and is then rendered completely sterile by passing steam in at the bottom and boiling the wort until the steam issues freely from the upper aperture. The apparatus is then closed hermetically, a vacuum being produced by the condensation of the steam. The vacuum is relieved by allowing sterilised air—filtered through cotton wool (*see* p. 150)—to enter; the maintenance of a slight pressure inside the vessel prevents the entry of germs. By stirring the starch and running cold water down the outer walls of the cylinder 1000 hectolitres of boiling wort may be cooled in five hours to 38°; this is the most suitable temperature for the *Mucor* fermentation, but a great part of the sulphuric acid added must first be neutralised. A vat of 1000 hectolitres capacity contains 150 to 200 quintals (15 to 20 tons) of maize and six times as much water.

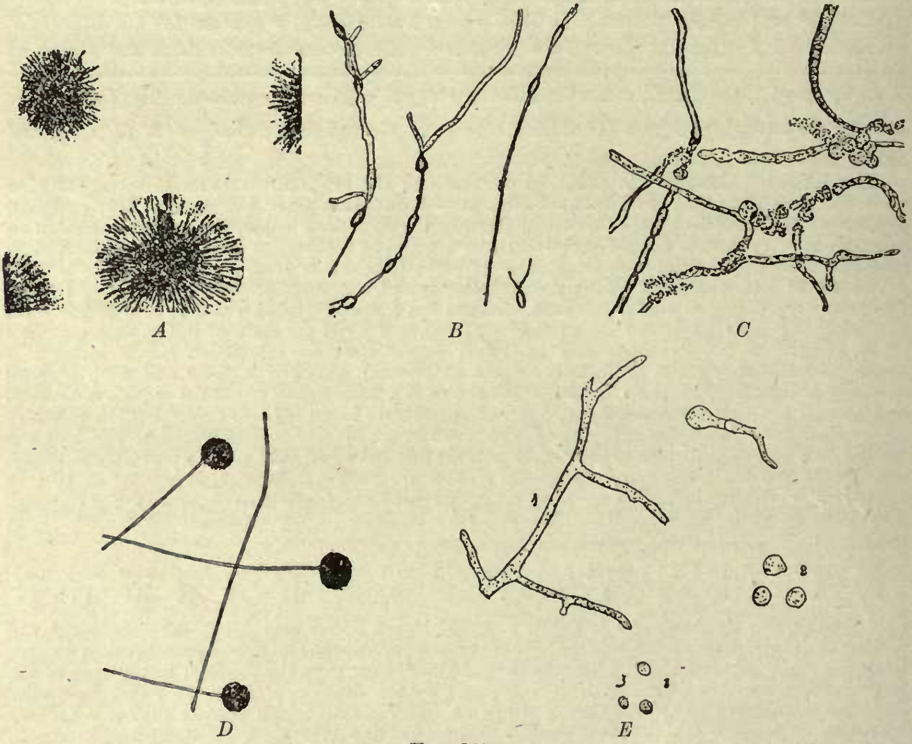

FIG. 127.

A. Colonies of *Amylomyces Rouxii* in wort-gelatine. *B*. Mycelial conidia of *Amylomyces Rouxii* in aerobic cultures. *C*. Segmentation into gemmæ of the mycelium of *Amylomyces* in anaerobic culture. *D*. Hyphæ of *Mucor* β (1 : 100) with sporangia in aerobic culture. *E*. Mycelium of *Mucor* β with spores in different stages of development in anaerobic culture: 1, spores just separated; 2, turgid spores ready to germinate; 3, germinating spores; 4, mycelium (1 : 600).

The *Amylomyces* is cultivated in the laboratory on 100 grams of rice and 200 c.c. of sterile wort, so that preferably spores are developed. Every culture-flask contains a total of about 0·1 gram of spores, and this quantity is sufficient to inoculate 1000 hectolitres of wort. The *Mucor* is introduced, under aseptic conditions, into the vats from above and the stirrer set in motion; a little air is introduced, this issuing by an upper tube with a hydraulic seal. In the course of twenty-four hours the wort is attacked by an abundant growth of the *Mucor*. The mass is then cooled to 33° and, in order to complete the alcoholic fermentation more rapidly, a small quantity of ordinary yeast (500 c.c. of a wort culture, corresponding with 3 to 4 grams of pressed yeast) is added.

After three to four days, the alcoholic fermentation is complete (the carbon dioxide passes out at the top through the water-seal). Fig. 128 shows diagrammatically a plant with five large fermentation vessels.

The advantages of the Amylo process are: (1) a considerable saving in malt, only about 1 per cent. being used instead of 12 to 15 per cent. by the old process; further, air-dried malt is difficult to keep in hot countries; (2) the reduction of the amount of yeast required to a minimum. The yield of alcohol is also sensibly increased, 100 kilos of maize containing 57 to 58 per cent. of starch yielding 37·5 litres of alcohol, *i. e.*, 65 (often 66) litres of pure alcohol per 100 kilos of starch; the old method of working gives only 60 to 61 litres.

The increase in the alcohol-yield is naturally due to the fermentation taking place in a wort uncontaminated with extraneous micro-organisms; on rectification, 4 to 5 per cent. more good spirit (*bon goût*) is obtained than by the old process.

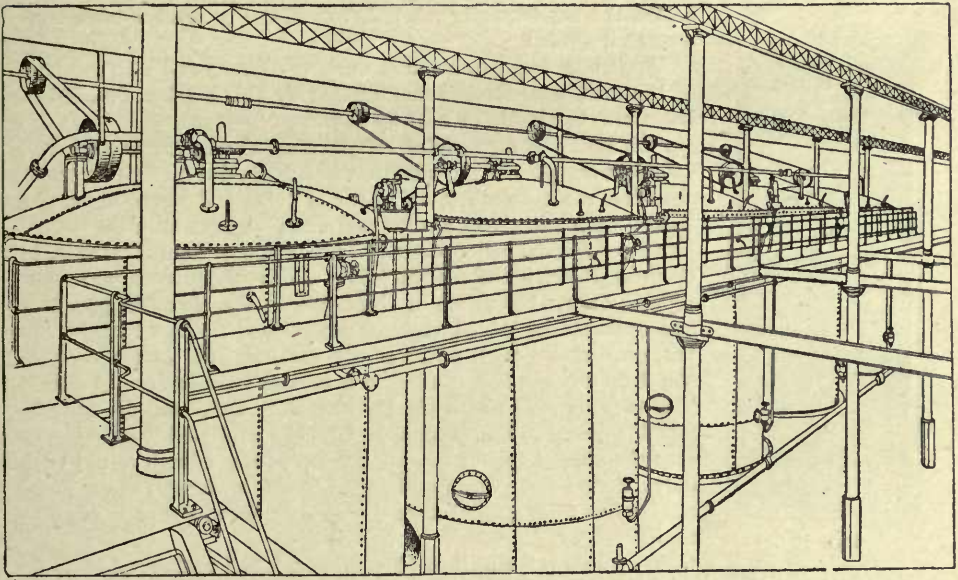

Fig. 128.

Finally, the spent wash (residue after distillation) filters better, since it contains less dextrin and does not block the filter-presses.[1]

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[1] In a German distillery the Amylo process was applied in 1912 in the following manner: 350 kilos of ground maize are treated for an hour at 60° with 1000 litres of water containing about 3 litres of hydrochloric acid free from arsenic. The mass is then steamed for forty-five minutes at 4 atmos. pressure in the ordinary Henze type vessel, the steam issuing from the air-cock. For twenty minutes the pressure is maintained at 4½ atmos., the steam being then discharged into another vessel so as to lower the pressure to 2 atmos., at which it is kept for fifteen minutes. Finally, under this pressure the stirred mass is forced into the fermentation vessel, into which also two similar amounts of steamed product and 150 litres of boiling wash-water are introduced. The boiling mass is kept mixed with a current of sterilised air, while the temperature is lowered to 40° by a water-spray applied outside. The mass is then seeded with a pure culture of Mucor Delemar, which multiplies rapidly at 35° to 38°, air being blown through for twenty-four hours. After a further period of thirty-six to forty-two hours without aeration saccharification is complete, a small quantity of selected alcoholic ferment being then added. This increases rapidly in twenty-four hours (with aeration) and after five to six days of active fermentation (without aeration) an attenuation of 0·5° Balling is reached. With the necessary precautions there is no danger of contamination, and the residual grains form an excellent cattle food. The consumption of coal for the whole process is 900 kilos per 1400 kilos of maize treated, and the yield is as much as 37·7 litres of pure alcohol per 100 kilos of maize.

DISTILLATION OF THE FERMENTED LIQUID. As has already been stated, the fermentation is rendered the more complete by using worts which are not too concentrated and yield 9 to 10 per cent. of ethyl alcohol. These fermented liquids contain also small quantities of various other substances, such as aldehydes, organic acids (acetic, propionic, butyric, lactic, succinic, etc.), certain higher alcohols (amyl, propyl, butyl, glycerol), etc., besides the solid residues of cereals and yeast and small amounts of unfermented dextrin and starch.

It was formerly not easy to separate the ethyl alcohol from these products, in spite of the great differences in boiling-point in some cases (amyl alcohol, 132°; ethyl alcohol, 78·4°), and, as already explained on p. 130, this separation cannot be effected with the most exact fractional distillation, so that recourse must be had to *rectification* (*see* p. 3).[1]

Every distillation apparatus is now composed of four parts: (1) the boiler in which the alcoholic liquid is heated; (2) the rectifier; (3) the dephlegmator; and (4) the condenser. The liquid collecting in the dephlegmator returns to the column (hotter), where alcohol vapours are formed richer than those from which it was formed in the first distillation; so that the alcohol vapours of the dephlegmator, uniting with the other vapours before the condenser is reached, contribute to form a more concentrated alcohol.

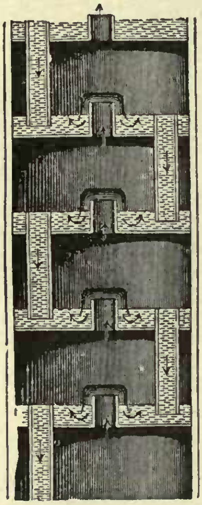

FIG. 129.

Apparatus with continuously working columns and with recovery of the heat were studied and applied by Coffey (Eng. Pat. 5974), but more thoroughly in 1867 by Savalle.

The action of a rectifying column may be understood from Fig. 129, showing part of the column, which is divided into a number of chambers communicating by means of tubes and placed above the boiler. The mixture of alcohol and water vapours from the boiling fermented wash below ascends the column from chamber to chamber through the central tubes, which are covered with caps dipping below the surface of the liquid in the chambers; by this arrangement the mixed vapours are obliged to pass through the hot, condensed liquid, which slowly descends the column through the drop-tubes, when it reaches a certain level in each chamber. The vapours give up to the liquid mainly water-vapour, and the liquid gives up to the vapours preferably the alcohol it contains, so that the alcohol-vapour reaches the top of the column mixed with only a little water-vapour and passes to the condenser, whilst water almost free from alcohol flows downwards, forming *vinasse* or spent wash.

With this column, 8 to 10 metres high and containing 20 to 25 plates or chambers, one distillation and partial rectification yield directly a crude 50 to 65 per cent. alcohol, and when this is subjected to a second similar distillation and rectification a concentration of 90 per cent. or even 96 per cent. is attained; each apparatus gives a high output. This is the procedure often adopted in France.

Taller columns (14 to 18 metres) are, however, used, especially in Germany, and these with efficient dephlegmators give 90 per cent. or even 96 per cent. alcohol in one continuous, although slower, operation. The *cylindrical* columns are advantageously replaced by

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[1] The first forms of distillation apparatus were used in the times of the ancient Arabs, and were termed *alembics*. The alchemists made improvements in the shape, especially of the part used for condensing. Simple distillation apparatus, like that used for obtaining distilled water (Vol. I., p. 253) yield a highly aqueous spirit, termed *phlegm*. Argand, and later Adam (about 1800), utilised the heat of the aqueous alcoholic vapours distilling over to heat the liquid to be distilled. Solimani and Berard (1805) improved the apparatus so as to allow a distillate moderately rich in alcohol to be obtained in a single operation. Before the condenser was placed a vessel called a *dephlegmator*, which condensed part of the water-vapour and part of the alcohol (*phlegm*), more concentrated alcohol vapours passing to the condenser. The first really rational and complete apparatus for the fractional distillation of alcohol was constructed by Cellier-Blumenthal (1815), who used dephlegmators and the first rudimentary rectifiers, but as early as 1813 A. Baglioni had placed semi-rectifying dephlegmators directly above the boiler.

The first column rectifying dephlegmator was devised by Derosne and Cail in 1817, and shortly afterwards widespread use was made of the very convenient Pistorius apparatus, with its flat, lenticular dephlegmators, which allows of 60 to 75 per cent. alcohol being obtained directly and is still used in some of the smaller distilleries.

square ones, which are less easily stopped up and more easily cleaned and repaired; in place of the costly copper columns, cheaper cast-iron ones are now largely used. A square plate of such a Savalle column is shown diagrammatically in Fig. 130, the apertures and tubes being sufficiently wide to avoid obstructions when dense fermented worts, rich in solid matters, are distilled. The heating of the column and of the liquid is no longer effected by direct steam, as this causes useless dilution; indirect steam is employed with a tubular heater, to be described later. In order to obtain regularity of working and constancy in the alcoholic strength an automatic steam regulator is used (*see below*), and the supply of fermented wash to the apparatus is so controlled that the yield and strength of the alcohol remain uniform. The heat of condensation of the alcohol vapours is recovered to heat the wash, and the latter, before being introduced into the top of the column, is passed through tubular heaters so as to utilise also the heat of the spent wash before this is discarded.

Fig. 131 shows the whole of a Savalle continuous distilling apparatus. The wash to be distilled passes from large constant-level tanks, situate on the upper floors, through the tube *m*, furnished with a regulating cock, 2, into the bottom of the heater, *C*, from which it issues at the top, after serving to condense the alcohol vapours coming from the column by the tube *k*; these vapours, however, first yield a little condensed spirit in *B*, this being carried to the column by the tube *r*. The heated wash passes along the pipe *q* to the top of the column and slowly descends, meeting meanwhile the ascending vapour current, to which it gradually gives up its alcohol, as stated above (*see* Fig. 129). The alcohol condensed in the wash-heater is cooled in the condenser, *D*, below, through which cold water circulates. If the wash is heated in the wash-heater sufficiently to form vapour, this passes into the small dephlegmator, *H*, whence the condensed alcohol and water are led by the tube *S r* to the column, whilst the alcohol vapour which is not condensed proceeds through *t* to the condenser along with the other alcohol. When all the plates of the column are covered with wash, steam is passed in from below by heating the exhausted vinasse by pipes from the heater, *G*, in which superheated steam from suitable boilers circulates; this steam is regulated by the tap *j*, which in its turn is controlled by the automatic regulator *F*. When the distilled alcohol issues from the test-glass, *E*, the access of wash through 2 is regulated so that the alcoholic strength remains constant. In the column the wash traverses a path more than 125 metres in length, the total absorptive surface being more than 200 sq. metres, so that every litre of wash, before exhaustion, meets a surface of vapour 200 metres long. In this way 30,000 kilos or more of wash may be distilled per day without interruption of the working for months.

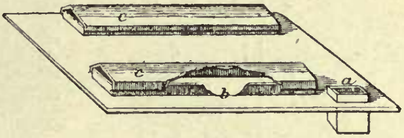

Fig. 130.

Fig. 132 shows Savalle's tubular heater more in detail. Steam under pressure from ordinary boilers traverses the regulator, *E*, and passes through the tube *i* to a large metallic cylinder, *G*, which contains a series of vertical tubes connecting the upper chamber, *G′*, with the lower one, *G″*; the latter is filled with almost exhausted vinasse supplied from the lower part of the Savalle column by the pipe *x*. The spent wash, which is already very hot, is thus easily brought into a condition of vigorous ebullition and loses the last traces of alcohol, which rise with a large quantity of steam through the pipe *y* into the Savalle column. The exhausted spent wash is discharged continuously from the tube 7, whilst the condensed steam issues from the tap 8.

Fig. 133 shows the *automatic regulator of the pressure* and steam in the distilling and rectifying column. In order that it may pass through all the layers of liquid on the plates of the column, the steam must be at a certain pressure in the column itself; this pressure increases or diminishes according as the quantity and temperature of the steam rise or fall, and the greater the supply of steam the more dilute will be the alcohol. If the column is connected with the pressure regulator by means of the tube *F* (*f* in Fig. 131), then, when the pressure increases, the water in the lower chamber, *A*, of the regulator is forced along the tube *B* to the upper chamber and raises a float, *C*, which operates the lever *D*, and so partially closes the tap (or valve) *E* controlling the supply of steam to the heater, *G*; owing to the diminished supply of steam the pressure falls. In the opposite case, when the pressure in the column is smaller than that necessary for regular distillation, so that the concentration of the alcohol (measured in *E*, Figs. 131 and 134) becomes too high and the yield too small, the water of the upper chamber of the regulator descends to the lower one, the float, *C*, hence falling and the steam-cock, *E*, opening a little. With these regulators, which are sensitive to variations of one-thousandth part of an atmosphere, the distillation is automatically regulated and requires very little personal control.

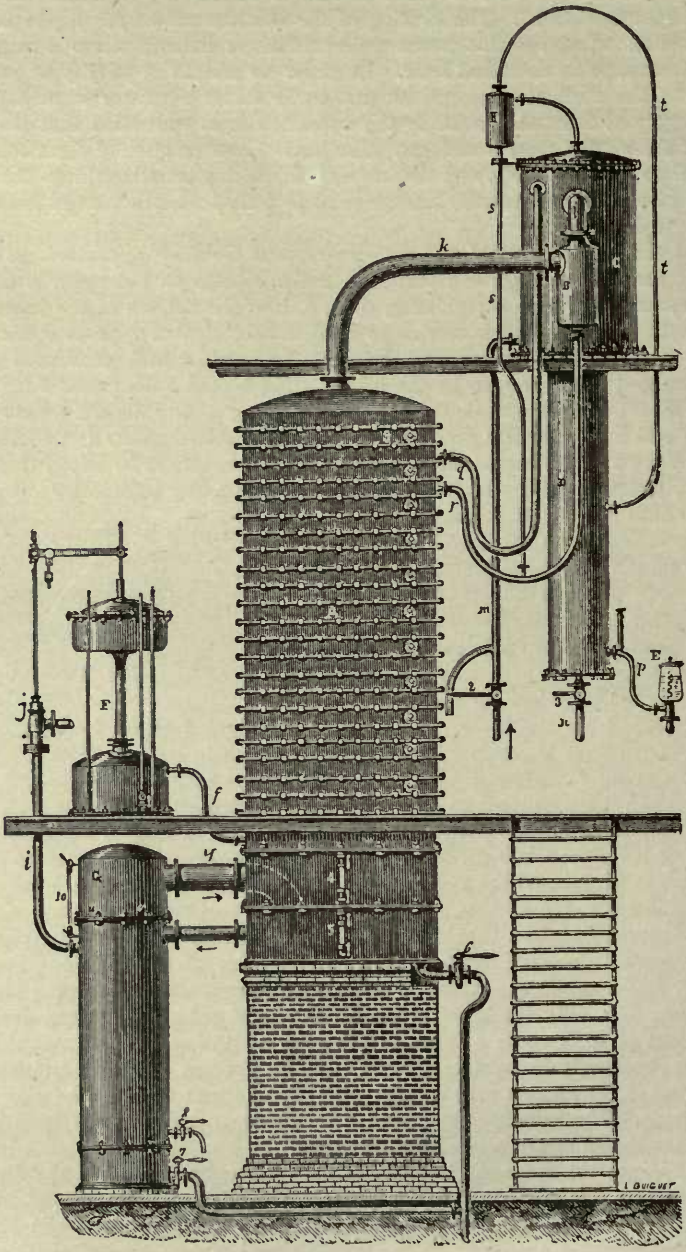

Fig. 131.

The constancy of the strength of the alcoholic distillate is controlled by the test-glass, *E* (*see* Fig. 134), which is situated in the alcohol discharge tube and contains an alcoholmeter fitted with a thermometer, so that the concentration and temperature are indicated continuously.

Of the variously highly perfected forms of apparatus (Ilgès, Coffey, Pampe, the last of which gives very pure spirit by distillation under reduced pressure) used in Britain, Germany, Russia, etc., which allow of the continuous and direct production of 90 to 96 per cent. alcohol without special rectification and refining (when the first and last products of distillation—*foreshots* and *tailings*—are kept separate; *see later*), we shall refer only to the apparatus of Siemens Brothers, which is largely used in Germany (Fig. 135); the new Kubierschky column is described later (*see* chapter on Tar Oils and Benzene). The Siemens column is composed of three principal parts: the heater (or pre-heater), *A*, the distillation column, *B*, and the rectifier, *C*; the whole is formed of superposed cast-iron discs or rings fitted with pasteboard packing and held tightly together by bolts extending from the top to the bottom. Inside are plates arranged spirally round a central tube, *D*, which passes about half-way up the column to *f*; the liquids thus traverse a long path, so that a large production is possible with a relatively small tower-space. The apparatus is also economical, since it is not necessary to construct it of copper. The heater, *A* (*see also* Fig. 136, *A*), contains, in the chambers *a* and *o*, hot spent wash which comes from the top of the column. Between these hot chambers are arranged alternately others in which circulates the cold wash or wine to be distilled; this is supplied through the pipe *d* by means of high-pressure pumps, and begins to be heated as it descends the spiral chambers between the hot ones containing the spent wash. When it reaches the bottom the hot wash passes into the central pipe *D*, and rises to the higher level, *f*, in the distillation column, *B* (which embraces the space between *d* and *E*). The pipe *D* empties on to the perforated spiral plates (*see* Fig. 136, *B*) and, as it descends, the wash meets a current of steam rising from the tube *o* through *B*. In this way the alcohol liberated from the wash rises with the steam through the perforations of the spiral plates and thus continually meets fresh quantities of wash and becomes continually richer in alcohol, as is shown in Fig. 136, *B*. The wash, thus deprived of alcohol, reaches the bottom as very hot spent wash, which,

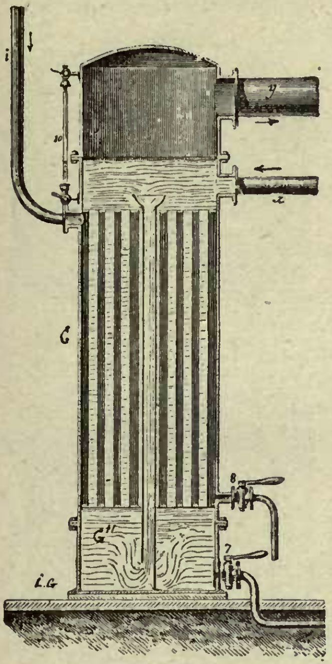

Fig. 132.

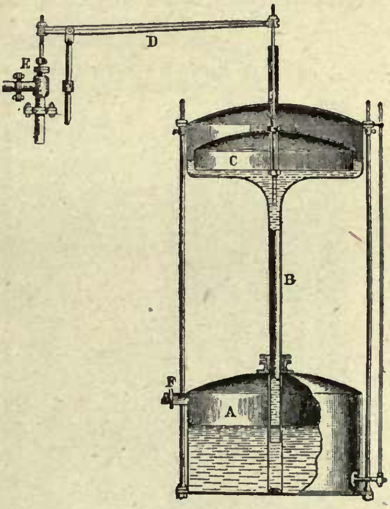

Fig. 133.

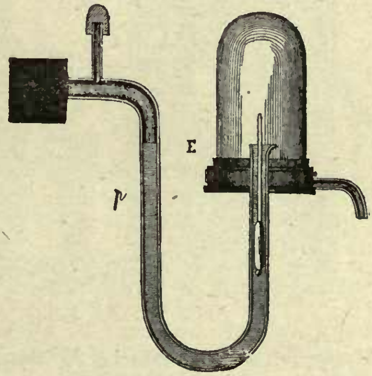

Fig. 134.

before leaving the column, traverses the chambers of the heater (shown in Fig. 136, *A*), and is then discharged continuously from the pipe *J K*, at a lower level than *f*. The mixed alcohol and water vapours enter the rectifying compartment, *E*,[1] which is formed of plain discs and is filled with wash, the level of which may be seen through suitable glass windows. The alcohol vapours rise into the rectifier, *C* (more properly termed a *fractionator* or *dephlegmator*, *see* p. 158), formed of non-perforated and hence non-communicating spiral chambers (Fig. 136, *C*), in some of which circulate the ascending vaporous mixture, whilst the alternate ones are traversed by a descending current of water; the latter is not very cold, as it comes from the top of the condenser, *S* (by means of the pipe *t*), so that it condenses mainly steam and only a little alcohol vapour, which falls into the distilling column again. The alcohol vapours gradually become more and more highly concentrated and pass through the tube *F* to the refrigerator, *S*, where they condense and are cooled by water flowing in at *s* and out at *t*. By means of a sample taken from the column *B* by the tube *p* and

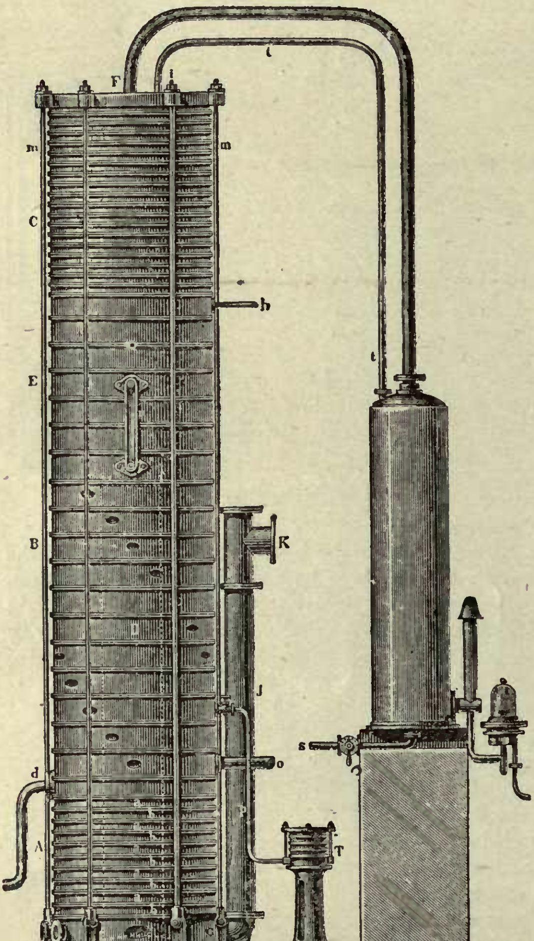

FIG. 135.

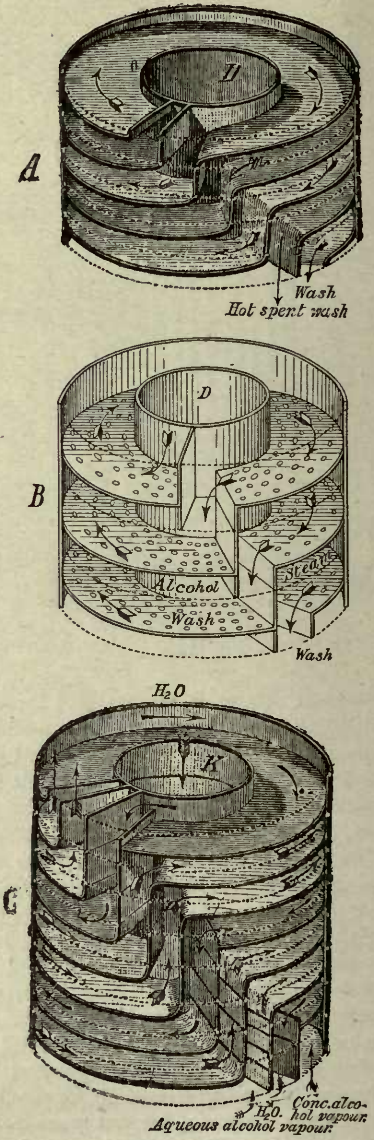

FIG. 136.

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[1] Pampe (Ger. Pat. 199,142, 1908) suggests placing, before the rectifying compartment, a steam-turbine with rapidly rotating vanes, which separate all the suspended drops or impurities from the vapours.

examined in the tester, *T*, it can be ascertained if the spent wash is completely free from alcohol.

In some cases it is observed that the spirit from such a cast-iron apparatus absorbs traces of hydrocarbons and of hydrogen sulphide which are formed from the iron and give an unpleasant taste and smell to the alcohol; this may, perhaps, depend on the quality of the metal and on the newness of the apparatus.

We shall mention finally the attempts which have been made, first by Perrier in 1875, to transform the vertical column into a horizontal distilling and rectifying column with a central rotating axis carrying helically arranged blades, which transport even a very dense wash from one end to the other, whilst the opposing current of steam removes the whole of the alcohol. The process was perfected by Sorel and Savalle (1891), who arranged the numerous vertical chambers of the horizontal column in a more rational manner. These forms are not yet free from disadvantages, but they have the advantage of being considerably more economical to construct and of bringing all the taps conveniently to hand on the same level.

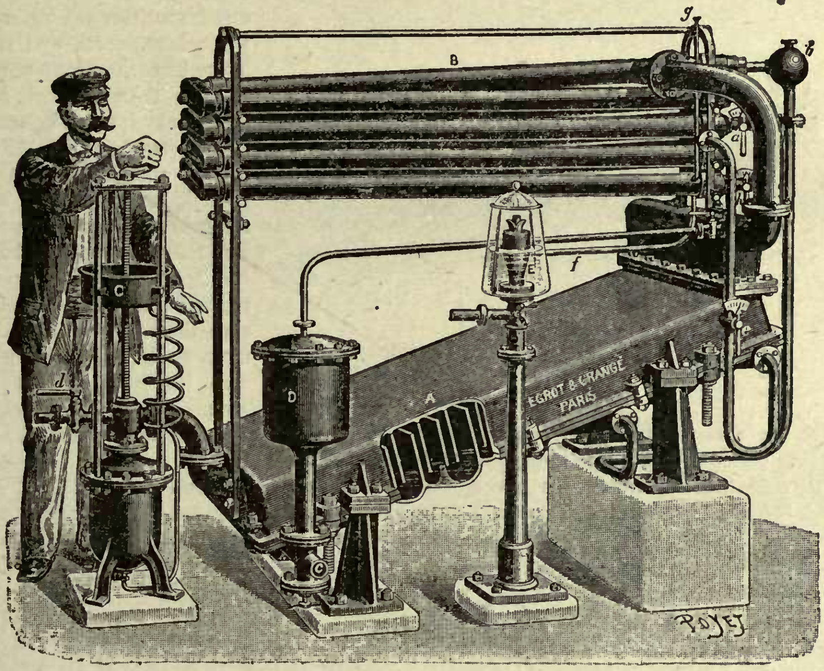

Fig. 137.

A, distilling column; *a*, entrance of the wash into the heater or refrigerator; B, condenser and heater; *b*, hot wash pipe; *C*, adjustable steam regulator; *c*, exit for spent wash; *D*, hot wash extractor used as heater; *d*, steam-cock; *E*, test-glass giving the strength of the alcohol; *e*, valve regulating flow and hence strength of the alcohol; *h*, entrance of water into refrigerators in case of need.

Lastly, Guillaume eliminated various defects of these columns and at the same time retained all their advantages by employing very simple and convenient inclined columns (made by Égrot, of Paris), which allow of very dense washes being employed without danger of obstruction. Fig. 137 shows the complete Guillaume-Égrot apparatus, and the description of the various parts given underneath will indicate the way in which it works. The cross-section shown in Fig. 138 gives an idea of the internal arrangement of the inclined column, and Fig. 139 represents the ground plan of the column, the arrows indicating the horizontal, zigzag course followed by the liquid from the highest part of the column, whilst the vapours ascend the column in a zigzag vertical path and bubble through the liquid in all the chambers formed by the numerous vertical partitions. With relatively small plant, which may be mounted on portable cars (*see later*), 30,000 litres or more of wash, containing 10 per cent. of alcohol, may be distilled per twenty-four hours, 90 per cent. alcohol being produced.

In the modern distillery the consumption of steam should not exceed 25 kilos (about 3 kilos of coal) per 100 kilos of wash, and the consumption of water in the condenser should not exceed 80 litres.

RECTIFICATION OF ALCOHOL. The alcohol obtained with the ordinary Savalle apparatus is not sufficiently concentrated or pure to be placed on the market, and even that obtained with other forms from washes which have not been fermented with selected yeasts should be freed by rectification and refining (*see later*) from various impurities which impair the colour, smell, and taste. These impurities may be more volatile than alcohol (such as aldehydes and certain esters) or less volatile (as acetic and butyric acids; propyl, isopropyl, and amyl alcohols; various esters, etc.), and they are separated from the *true alcohol* if, in the redistillation and rectification, the portions which distil most readily (*foreshots*) and also the least volatile portions (*tailings* or *fusel oil*, which has a very disagreeable odour if obtained from potatoes, molasses, or maize, but a pleasing odour if derived from grapes, fruit, etc.) are kept apart.

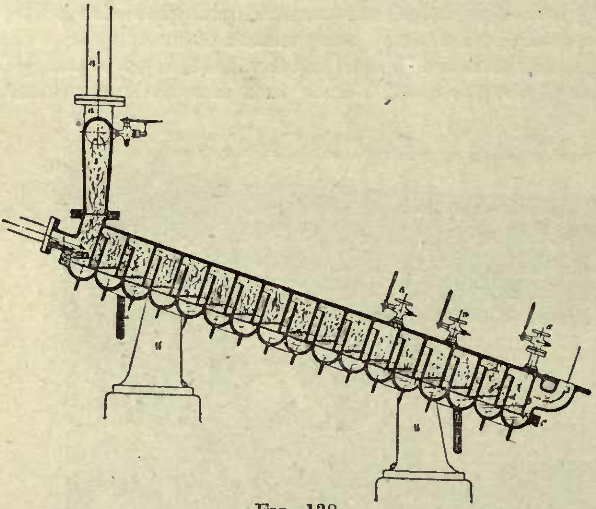

Fig. 138.

Rectification apparatus usually consists of a large copper or iron boiler, *A* (Fig. 140), which is heated with an indirect steam-coil and on which is mounted the copper rectifying column, *B*. Above this and to one side is a large dephlegmator, *C*, which serves as a heater, and is of importance not so much for condensing the less volatile products (water, amyl alcohol, etc.) as for furnishing a continuous and abundant supply of a suitable alcoholic liquid to wash the vapours arriving at the top of the column; it is, however, quite useless to employ several dephlegmators, as was erroneously done in the past. The foreshots, which have a concentration up to 94 per cent. and boil at 85°, are collected separately. Then from 85° to 102° alcohol passes over. The tailings, boiling above 102°, are collected in the bottom of the column by shutting off the steam and thus emptying the plates. The quantities of these products vary according to the quality of the alcohol required; thus 20 per cent. of foreshots and tailings may be obtained and 80 per cent. of alcohol (*bon goût* extra), or 5 per cent. of foreshots and tailings and 95 per cent. of alcohol (*bon goût*).

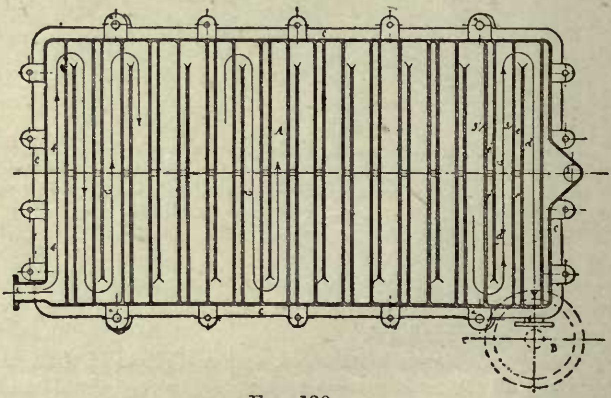

Fig. 139.

This apparatus does not work continuously, the boiler requiring to be discharged and recharged. Attempts to render the process continuous were met with success in 1881

(E. Barbet), in spite of the difficulty of separating the pure alcohol from an impure product that boils below it and another that boils above it. This is effected by carrying out the operation in two phases, which are, however, continuous; in the first phase the foreshots are driven off and the alcohol distilled from the remaining liquid, the tailings being left behind. The boiler is then replaced by a rectifying column, which receives the impure product and distils the foreshots, passing the residue continuously at a certain height to a second lower column at the side; this distils and rectifies the pure alcohol and retains in the lowest chamber of the column the tailings, which are continuously discharged.[1]

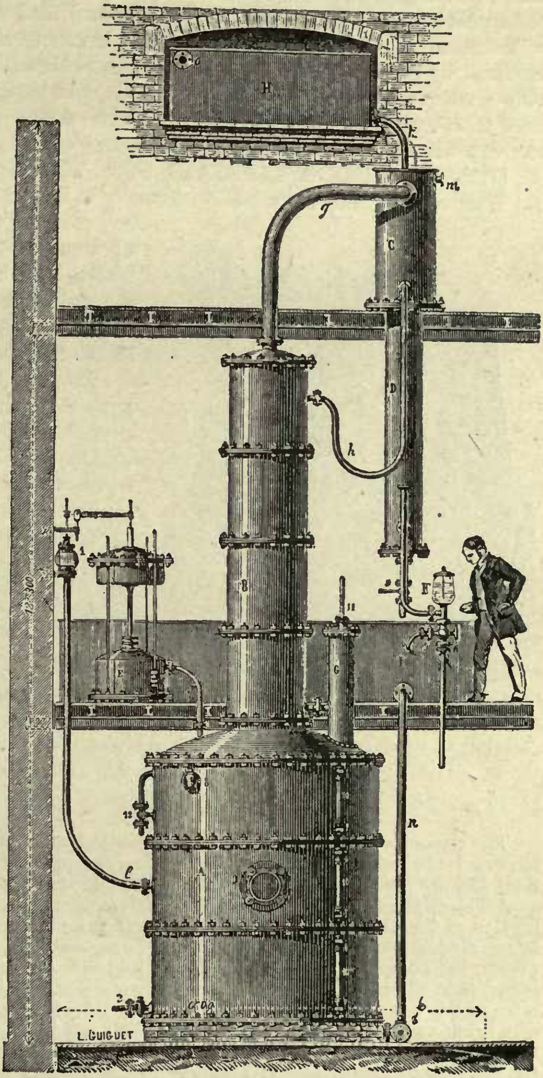

Fig. 140.

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[1] The tailings vary somewhat in percentage composition: water, 14 to 24; ethyl alcohol, 15 to 45; normal propyl alcohol, 6 to 14; isobutyl alcohol, 10 to 25; amyl alcohol of fermentation, 10 to 40.

The fusel oil is separated from the tailings by addition of a saturated salt solution and then forms a more or less yellow oil, which has the unpleasant odour of amyl alcohol and excites coughing; its specific gravity is about 0·83 and it boils between 80° and 134°, mainly at 130°. It varies in composition and contains principally amyl alcohol (especially that obtained from molasses), together with different proportions of normal propyl and isobutyl alcohols, caproic, caprylic, capric, acetic, and butyric acids, esters, furfural, and certain bases, besides 8 to 10 per cent. of ethyl alcohol.

The percentage compositions of two samples of fusel oil obtained (*a*) from potatoes and (*b*) from grain, are as follows: normal propyl alcohol, 6·854 (*a*), 3·69 (*b*); isobutyl alcohol, 24·35 (*a*), 15·76 (*b*); amyl alcohol, 68·76 (*a*), 75·89 (*b*); fatty acids, 0·011 (*a*), 0·16 (*b*); esters of fatty acids, 0·02 (*a*), 0·305 (*b*); furfural, bases, etc., 0·005 (*a*), 0·021 (*b*) (G. Boobey, 1913).

Owing to its poisonous properties, fusel oil must be denatured before being sold in Italy, so that it cannot be added to alcoholic beverages.

Fusel oil is now largely used for the preparation of amyl alcohol, which is used in the manufacture of fruit essences (*see later:* Amyl acetate), for obtaining nitrous and other ethers, and for gelatinising explosives (nitrocellulose); during the last five years the price of fusel oil has risen from 65 to 170, and even 195 lire per quintal. Pasteur thought that the *amyl alcohol* (iso- and d-amyl) arose from the action of specific bacteria on the sugar, but in recent years F. Ehrlich has thrown doubt on the formation of an alcohol with a branched chain from a sugar with a direct chain, and has now shown that it is the proteins of the malt and their decomposition products which furnish nitrogen to the yeast for the synthesis of its protein constituents and at the same time form amyl alcohol. In fact, in the fermentation of a pure sugar, Ehrlich obtained a quantity of fusel oil *proportional* to the quantity of *leucine* added; he was also able to obtain an amount of fusel oil equal to 7 per cent. of the alcohol formed (the usual amount being 0·4 to 0·6 per cent.) and, further, he succeeded in reducing the formation of fusel oil considerably by the addition of ammonium salts. The United States imported 2100 tons of fusel oil in 1910 and 2740 tons (£236,000) in 1911.

In the Savalle rectifiers 45 kilos of coal are consumed per hectolitre of pure rectified alcohol. Continuous rectification results in a saving of almost 50 per cent. of fuel compared with the discontinuous process. During rectification the loss of alcohol is 1 to 2 per cent., and the cost of rectification varies from 3 to 3·5 lire (2*s*. 6*d*. to 3*s*.) per hectolitre. The firm of Savalle holds that it is more economical to use cold air than water in the refrigerators of the condensers.

Attention may lastly be drawn to the ingenious although complicated Perrier distilling and rectifying apparatus, in which the vapours of alcohol, water, higher alcohols, and aldehydes are passed successively into columns filled with glass beads and surrounded by a jacket containing a liquid boiling at a constant temperature, the latter being hence assumed by the whole of the tower. In one of these, having a temperature of 85° to 90°, only water and the tailings are condensed; the vapours then pass into a second tower, kept at 75°, where all the ethyl alcohol (which may be rectified in another tower) separates; the vapours from this form the foreshots and are condensed in a succeeding tower.

OTHER PRIME MATERIALS FOR THE MANUFACTURE OF ALCOHOL.

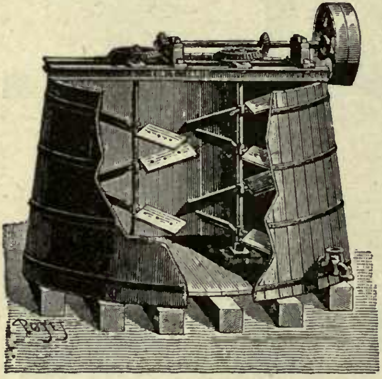

Fig. 141.

(1) **Beetroot and Molasses.** It is especially in France that considerable quantities of beet are used for the manufacture of alcohol instead of sugar; this is never done in Germany or Italy. The beets are washed and minced, and the pulp exhausted by pressure, maceration, or diffusion with water. This treatment is described in the section on *sugar*.

The spirit obtained from the beet is less pure than that from potatoes, containing more propyl and butyl alcohols but less amyl alcohol.

Of more importance in Italy and various other countries is the utilisation of *beet-molasses*.[1]

The complete fermentation of molasses has presented many difficulties, which have now been overcome. Formerly, after the molasses was diluted to 8° to 10° Bé. (this was carried out in vats provided with stirrers, *see* Fig. 141), it was slightly acidified with sulphuric acid [2·5 grams of free H_2SO_4 per litre. E. Legier (1913) replaced the sulphuric acid advantageously by a smaller amount of hydrochloric acid, pure yeasts acclimatised to worts containing traces of formaldehyde being used], as the reaction is usually alkaline. The liquid was then boiled for some hours in a current of air in order to eliminate the volatile acids (nitric, etc.) liberated, and, after cooling it to 15°, alcoholic fermentation was initiated by the addition of vigorously fermenting

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The annual output in Germany is estimated at about 1000 tons, and in 1912 Germany imported 124 tons and exported 197 tons. The price at one time was very low: in 1911 less than £28 per ton, in 1905 £70, in 1910 £100, and in 1913 £144.

[1] This is the dense, viscous, and blackish mother-liquor which remains from the final crystallisation of the sugar (*which see*) and from which no further sugar will crystallise, although 45 to 50 per cent. is present (*see* explanation in the section on Sugar); it has a density of 40° to 45° Bé. (74° to 84° Balling). The composition of beet-molasses is as follows: water, 16 to 20 per cent.; sugar, 44 to 52 per cent.; non-nitrogenous extractive matters, 10 to 15 per cent. (largely pentoses); nitrogenous compounds, 6·5 to 9·5 per cent. (of which only one-third consists of proteins, the rest being amino-acids); ash (deducting CO_2), 8·5 to 11 per cent. In Italy the working-up of molasses has assumed considerable importance during the last few years, owing to a change in the method of taxing sugar; previous to 1903, sugar recovered from molasses by somewhat expensive processes (*see* Sugar) was exempt from taxation, whilst nowadays all sugar produced is taxed uniformly, so that the manufacturers find it advantageous to sell the molasses to the distillery at £2 8*s*. to £3 4*s*. per ton (pre-war price). In 1907 the Italian distilleries used 38,000 tons of molasses, obtaining 97,330 hectolitres of alcohol, while in 1912 125,000 hectolitres were obtained from 56,000 tons.

In Germany, Belgium, and part of France, it is found to be more convenient and rational to utilise a large proportion of the molasses as cattle-food after absorbing it by highly porous vegetable substances. In Italy, *tumelina*, patented by E. Molinari, and *sanguemelassa* (blood-molasses), patented by L. Fino, are manufactured; the residues of dried tomatoes (Squassi, Bono) and various other dried industrial products are now used as absorbents. In Germany more than 150,000 tons of *molassic fodder* are consumed; Italy produced 40,000 tons in 1908 and more than 48,000 in 1909.

liquid and the excess of acid which forms gradually neutralised with chalk. The spirit thus obtained is difficult to purify, as it contains an aldehyde and various acids which boil at very low temperatures.

To-day, however, the process is much more simple, as Jacquemin and Effront have devised various methods of preparing races of yeast capable of living actively in worts rich in salts (nitrates, carbonates, etc.), such as those prepared from beet-molasses. In the past the difficulty of fermentation was attributed to the presence of nitrates, but it appears from Fernbach and Langenberg's experiments (1910) that nitrates, even in proportions as great as 0·3 per cent., facilitate fermentation.

(*a*) In the Jacquemin process the fermentation is initiated in small quantities of wort in suitable vessels (*see* Fig. 125, p. 150), and the wort of the last rather larger vessel (into which is also placed a little hydrofluoric acid, to which the yeast has been previously "acclimatised") serves to pitch a 200-hectolitre vat containing diluted, non-sterilised molasses, to which has been added 8 to 10 kilos of calcium hypochlorite, this preventing the development of heterogeneous organisms during the first few hours without damaging the yeast—already adapted to chlorine. By means of this vat two other 500-hectolitre vats of similar diluted molasses may be brought into a state of vigorous fermentation; the fermentation takes place so rapidly (and this is the most specific action of these yeasts) that in three days the whole of the molasses is fermented, there being thus no time for the development of extraneous germs causing harmful secondary fermentations.

(*b*) The Effront process is still more simple, and is based on the use of selected yeasts specially adapted to molasses worts and endowed with exceptionally rapid fermenting properties; these yeasts are placed under such conditions (namely, the addition of resin) [1] that they easily overcome deleterious bacteria and complete the fermentation before these become harmful. To the molasses simply diluted with water and not sterilised are added these special yeasts, together with 1 kilo of colophony per 10 hectolitres of wort; in three days the fermentation is complete. In 1903 almost 1,000,000 kilos of colophony were used in France for this purpose.

In general bottom fermentation beer yeasts (*see* Beer) give high yields of alcohol.

(2) **Alcohol from Fruit.** This is not of great industrial importance, although in certain districts and in certain years it assumes considerable magnitude. In Italy, dried figs of little commercial value, carobs, etc., are used; and, in other countries, plums, apples, pears, etc. These fruits often give an irregular, and seldom a complete, fermentation, owing to conditions similar to those encountered with beet-molasses. Hence, as in the latter case, use is made of very active yeasts adapted, where possible, to these special worts.

The alcohol obtained from these worts has a characteristic odour indicating its origin.

(3) **Alcohol from Woody Substances.** This is a subject which has aroused considerable interest during about the last twenty-five years. Many attempts have been made to transform a part of the wood (sawdust, peat, etc.) into fermentable sugar by the action of acids (HF, SO_2, H_2SO_4, etc., at 170° and 16 atmos. pressure) on the matter (lignin) encrusting the wood and not on the cellulose. In Chicago the process was applied on a

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[1] Effront observed that the *law of the strongest*, which is often verified in bacteriology—the most numerous and powerful bacteria rendering life impossible to weaker ones—scarcely ever holds in the case of alcoholic fermentation, where, even though the harmful bacteria are less numerous than the yeasts, the latter are seldom victorious, the bacteria often entirely arresting alcoholic fermentation even when the conditions are favourable for the latter.

According to Effront, this is owing to the different specific gravities possessed by yeasts and bacteria, which hence live in different, relatively distant strata, so that there is no opportunity for the application of the law of the strongest—which consists in the production by certain micro-organisms of poisonous substances preventing other forms from developing. Effront hence proposes to add suitably emulsified resin (colophony) to the worts at the beginning of the fermentation; this has the property of coagulating only the bacteria, which become denser and are brought into more intimate contact with the yeast, the latter then being in the most favourable condition for the annihilation of the bacteria. The resin itself is not the cause of the death of the bacteria, as Effront states that these may be readily cultivated in the pure state in presence of resin (private communication).

vast industrial scale according to A. Classen's patents (Ger. Pats. 130,980, 1899, and 161,644, 1904).[1] 100 kilos of wood (with 25 per cent. of moisture) are treated in an

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[1] As early as 1820, Braconnot observed that sugar is formed when wood or even cotton cloth is treated with sulphuric acid. Later on Melsens obtained a good yield by treating cellulose with dilute sulphuric acid in an autoclave under pressure. In 1860 Pettenkofer investigated this process and showed that it could not, at that time, compete with the use of potatoes. Still later, Basset prophesied a yield of 32 per cent. of alcohol from the similar treatment of wood (!). Simonsen, in 1889, treated wood under pressure with dilute sulphuric acid (100 parts of water, 16 of wood, and 0·5 of sulphuric acid at 180° for two hours), transforming 25 per cent. of it into sugar (78 per cent. of which was fermentable) and obtaining a practical yield of 6 to 7 litres of pure alcohol; no industrial plant was, however, erected.

Reiferscheidt (1905) overcame the resistance of the wood to penetration by liquid acid (met with also by Classen) by causing sawdust to absorb two-thirds of its weight of sulphuric acid (sp. gr. 1·65) and subjecting the mass to the maximum pressure of a hydraulic press; simple digestion of the mass with water and filtration gave a fermentable liquid and a yield of 6·5 per cent. of alcohol on the weight of wood (pine, containing 53 per cent. of cellulose) taken. A similar yield is obtained by treating the wood with five times its weight of 1 per cent. sulphuric acid solution at a pressure of 8 atmos. for fifteen minutes. He confirmed the observation that the pentosans of the wood do not ferment, and with pure cotton he obtained as much as 12 per cent. of alcohol.

The use of concentrated sulphuric acid (66° Bé.) in the cold has also been suggested, a yield of more than 10 per cent. of alcohol (?) being claimed. Experiments have likewise been made on the treatment of wood in the hot with solutions of aluminium chloride, which at 100° to 105° dissociates with production of HCl, this converting the cellulose into dextrin and then into fermentable dextrose.

According to Th. Körner, the addition of oxidising agents or of ozone, as was suggested by Roth and Gentzen (Ger. Pat. 147,844, 1905), is of no advantage. He obtained the best yields by heating sawdust, straw, etc., with 0·5 per cent. sulphuric acid for two hours in an autoclave at 6 to 8 atmos.; only a small part of the molecular complex of the cellulose is converted into fermentable sugar, and he obtained a yield of alcohol equal to 15 to 18 per cent. of the weight of the true cellulose in the wood. Without the addition of sulphuric acid, the yield was about one-fourth less.

F. Ewen and H. Tomlinson, of Chicago (U.S. Pat. 938,308, 1909), treated 400 kilos of sawdust, straw, or stems of various cereals (with 30 per cent. of moisture) in autoclaves with 5 kilos of sulphuric acid of 60° Bé. diluted with 20 litres of water; after complete digestion and agitation the temperature of the mass is brought in fifteen minutes to 135° to 160° by means of steam under pressure; after half an hour the temperature is lowered rapidly to 100° by allowing the steam to escape, and the sulphuric acid then separated in the usual way. By this means 20 to 30 per cent. of the weight of the cellulose is transformed into fermentable sugar. Later, part of the sulphuric acid was replaced by sulphurous acid (1 per cent. on the weight of wood). A similar process is that of Eckström (Norw. Pat. 17,634, 1907). Willstätter obtained better results with hydrochloric acid in the cold.

Classen's process, which has been tried on a large scale in North America, has exhibited various disadvantages: the time required for treating 2 tons of wood was as much as six hours, the consumption of sulphuric acid was large, part of the sugar was destroyed, and frequent repairs were necessary. The process was improved by Ewen and Tomlinson, and was worked by the Standard Alcohol Company in a works at Georgetown, S. Carolina, and then by the firm E. J. Du Pont de Nemours. Less acid was used and the treatment maintained only for forty minutes, the autoclave being rotatable and made of steel protected outside with fireclay. This was filled with sawdust, sulphur dioxide (1 part per 100 of dry wood) being then passed in, and subsequently steam at 7 atmos. After forty minutes, the vapours of water, acetic acid, terpenes, and sulphur dioxide are passed into washing or absorption vessels, while the residual darkened sawdust is extracted with hot water: the aqueous extract is neutralised with chalk, filtered, fermented, and distilled. Rectification yields 94 per cent. alcohol free from methyl and higher alcohols, and containing only traces of furfural and other aldehydes. The cost of this alcohol seems to be less than three-halfpence per litre of 90 per cent. concentration.

Of the different works which attempted the manufacture of alcohol from wood the only one remaining at work in the United States in 1913 was that at Georgetown, where 200 tons of sawdust and wood waste from three neighbouring sawmills was treated daily; the yield of anhydrous alcohol amounted to 6000 litres per day (*i. e.*, about 3 per cent.), and even with the Simonsen process the yield did not exceed 5 per cent. However, the process was further modified by a return to Simonsen's system, but with less water and acid, the pulp obtained being subjected to diffusion and the sugar solution thus formed fermented, a liquid containing 2·5 per cent. of alcohol resulting.

J. Ville and W. Mestrezat (1910) state that, whilst cellulose resists dilute solutions (up to 30 per cent.) of hydrofluoric acid, with 50 per cent. solutions, 100 grams of cellulose yield 50 grams of glucose!

There has been much discussion recently (1906–1907) concerning a process for extracting spirit from *peat* in a manner similar to that described for wood. These attempts date from 1870, and various patents were filed in 1882–1891. The most important tests were made in Norway in 1906 by the Reynaud process (1903), in which 300 kilos of peat were treated in the hot with 700 kilos of water containing 7 kilos of sulphuric acid (66° Bé.) under 3 atmos. pressure; 600 litres of liquid were thus obtained and this was fermented with specially selected yeasts autoclave for an hour with about 100 kilos of aqueous sulphur dioxide and sulphuric acid in presence of steam at 6 to 7 atmos. pressure (150° to 165°). The excess of sulphur dioxide is eliminated by means of a current of air, the residue being boiled with water or extracted in diffusers, and the liquid neutralised with calcium carbonate and fermented. It is stated that wood thus yields a product containing 35·36 per cent. of solid residue, 34·63 per cent. of water, 10·97 per cent. of fermentable reducing sugar, 3·21 per cent. of non-fermentable reducing sugars (pentoses: xylose, etc.), 0·35 per cent. of sulphuric acid, and 0·77 per cent. of other acids, and it was hoped to obtain about 8 litres of alcohol (per 100 kilos of wood) mixed with a little acetic and formic acids, the residues being in part utilisable for making paper. The actual yields did not, however, correspond with expectations. Host and Wilkening (1910) improved the Flechsig process (1883) by treating 5 parts of cellulose first with 50 parts of 72 per cent. sulphuric acid at 20° for three hours, then diluting with water to obtain a clear solution with an acidity of 3 per cent., and heating this in an autoclave at 120° for two hours; in this way a yield of dextrose equal to 90 per cent. of the theoretical yield was obtained and, after fermentation, the corresponding amount of alcohol. In France, England, the United States and Canada, there has been an uninterrupted series of trials and failures during the past twenty years, some of the industrial processes being apparently based on speculation and hence certain of failure.

Woods of all kinds give the same yield of alcohol, with the exception of oak, which gives less owing to its content of tannin; the latter should therefore be eliminated beforehand.

(4) **ALCOHOL FROM THE SULPHITE LIQUORS OF PAPER WORKS.** According to the Swedish patents of J. H. Vallin and of Eckström, alcohol is obtained by treating the *waste sulphite liquors of paper-mills* in the hot with sulphuric acid and fermenting the liquid containing the glucose formed. The hot acid liquid has to be neutralised *almost* completely with chalk and decanted, the residue being then pressed in a filter-press; the liquid is then cooled on piles to 30°, pitched with yeast, aerated during fermentation (five to six hours) and the dilute alcoholic liquid (0·7 to 0·8 per cent. alcohol) distilled. From 10 cu. metres of the sulphite liquors are obtained 60 litres of 100 per cent. alcohol (which is, however, of bad flavour and is used for denaturation). For a factory producing 60 tons of cellulose per day, *i. e.*, 600 tons of waste sulphite liquors, the cost of tanks, pumps, piles, distilling apparatus, filter-presses, etc., may be taken as about £6000, and the alcohol produced (36 hectolitres per day) would cost (including all expenses, but excluding taxation) 10*s*. to 11*s*. per hectolitre at 100 per cent. strength. The problem of the disposal of the waste liquors (which contaminate the rivers) of paper-mills is not, however, solved in this way, since the liquid still contains much decomposable organic matter after the distillation of the alcohol.

In 1910 there were two factories in Sweden for the manufacture of alcohol from these *waste sulphite liquors:* that at Billingfors prepared *methyl alcohol* (15 kilos per ton of wood pulp) by H. Bergstrom and H. Fahl's process; the other at Skutskür manufactured ethyl alcohol. For every ton of cellulose there are obtained 8 to 9 tons of sulphite liquors containing, either dissolved or suspended, as much as 12 per cent. of organic substances, and yielding alcohol at less than 1½*d*. per litre. These yields and costs were confirmed in 1911 at the Spritfabrick Köpmanholmen, without allowing for the recovery of lime and sulphur from the residues. In 1912, three large Swedish sulphite cellulose works, using a modified process by G. Ekström, produced altogether 20,000 hectolitres of anhydrous alcohol in the year. According to Rinman's process, based on the dry distillation of the residues from the sulphate treatment of cellulose, it appears possible to obtain acetone, together with a little methyl and ethyl alcohols. During the European War, Sweden sold considerable quantities of this alcohol at high prices to the belligerent nations. In normal times, however, owing to the enormous bulk of the very weak alcoholic liquid (0·7 per cent.), the high cost of plant, and the large consumption of fuel necessary, such a process is workable only in countries where the conditions are exceptionally favourable.

(5) **Alcohol from Wine, Lees, Vinasse, and Withered Grapes.** In seasons when wine

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(*Saccharomyces ellipsoideus*), the yield being 25 litres of burning spirit at an inclusive cost of about 4·5*d*. per litre, which is about double the cost of that obtained from ordinary starchy materials. In 1905, the Danish Government offered a prize for the improvement of this process, but the yield was not increased, although it varies somewhat (6 to 8 per cent.) with the quality of the peat; in all cases the alcohol obtained in this way is too costly.

is abundant and prices low and in general when there are spoilt wines (at 6*s.* to 8*s.* per hectolitre), it is convenient to extract the alcohol from them, this being of use in the preparation of liqueurs and spirits.

The distillation presents no difficulty and is carried out either in the large distilleries or with a Guillaume-Égrot apparatus (*see* p. 163), which is mounted on a car so as to be readily transportable, and may be used in places where there is little available water, since the coolers and condensers act as heaters and are fed with the wine to be distilled. It gives directly 90 to 94 per cent. alcohol.

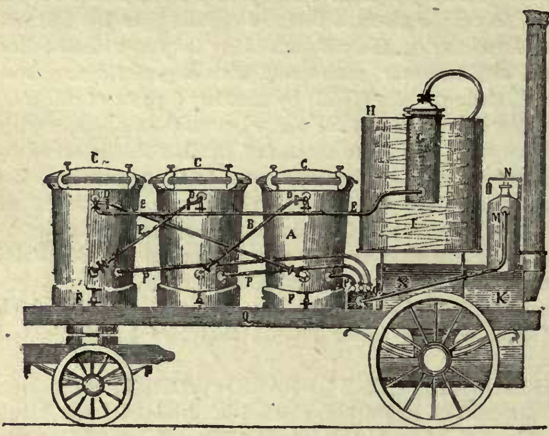

FIG. 142.

In the same way as wine, fresh lees or bottoms from wine vats (containing 4 to 6 per cent. of alcohol) and *dried grapes* [1] are treated.

The distillation of *vinasse*, containing 2·25 to 3·5 per cent. of alcohol, is of considerable importance in Italy; if this were all distilled it would yield about 250,000 hectolitres of pure alcohol annually (for a production of 40 million hectolitres of wine). Of the various forms of apparatus for the distillation of vinasse only those of Villard-Rottner and of Égrot will be described, as they are the commonest and differ little from other good types.

The generator, *K* (Fig. 142), of the Villard-Rottner apparatus sends steam from the dome, *M*, into the three boilers, *A*, in succession, the steam entering at the bottom and issuing at the top of each. These three boilers contain the vinasse mixed with an equal volume of water. The vapours, which are rich in alcohol, pass through the pipe, *E*, to the dephlegmator, *G*, and are then condensed in the coil, *I*, at a concentration little exceeding 50 per cent. When the first boiler is exhausted it is emptied and again charged, the steam passing meanwhile through the second and third; the first boiler now becomes the third, the second being then emptied, so that two boilers are always in use. The hot water from the boilers is treated separately for the extraction of tartar (*see this*).

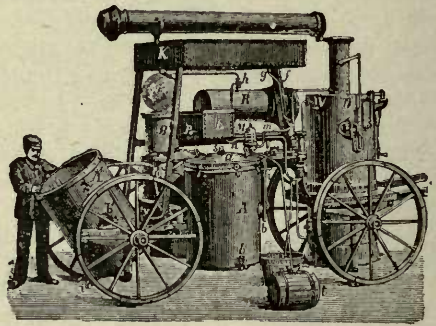

FIG. 143.

In the Égrot apparatus (Fig. 143) the boilers, *A*, are arranged on pivots, so that they can be inverted and rapidly emptied. Steam from the boiler, *D*, extracts the alcohol from the three boilers, which are arranged in series, as before, so that two are always in use while the third is being emptied and recharged. The alcohol vapours pass into the dephlegmator, *B*, and thence into the spherical rectifier, *C*; *R* acts as a condenser and is cooled by water from the tank, *K*. The condensed alcohol passes along

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[1] In some countries—at certain times in Italy—dried grapes are used for the production of alcohol, especially Greek grapes, which are received from viticulturists by the Greek Government in payment of taxes, and are dried and placed on the European markets. These grapes are first macerated in tepid water, then crushed and fermented in the usual way; the *wine* obtained may be used for mixing with other wines or for distillation. In 1905–1907, in order to help the crisis in the South, the Italian Government granted a considerable rebatement of taxation on the alcohol obtained from grapes. The Italian distillers then began to import large quantities of Greek grapes (containing 50 to 55 per cent. of sugar), which could be delivered in the factory at about £6 10*s.* per ton, so that the southern viticulturists reaped no advantage from the rebate, which was hence abolished.

the tube, *m*, to the test-glass, *M*, and from there to the casks, *t*, at a concentration of 55 to 60 per cent.

With the first apparatus, to treat 10 tons of vinasse, yielding about 8 hectolitres of brandy at 51 per cent., roughly 26 cwt. of coal are consumed, whilst the Égrot apparatus uses much less than this for an equal yield. The brandy thus obtained has almost always a rather unpleasant flavour, and is often used for rectification in the ordinary way (if too dilute it becomes opalescent), and is then left to age in oak casks so as to acquire a pleasing aroma. This result is obtained more rapidly by *pasteurisation*, that is, by passing the brandy through a coil surrounded by water at 60° to 65°, or by passing a current of ozonised air through it (*artificial maturation*). The name *cognac* is given to the finest old French brandies.

Alcohol from cereals may be distinguished from that obtained from wine, etc., as the latter always contains aldehydes (*see later*, Rimini's Reaction and Schiff's Reagent).

(6) **Alcohol from Green Maize.** Use has been made in the United States of the Stewart process, according to which the cobs are removed from the maize plants when the grain has attained a milky consistency. The remaining plants continue to grow and become exceptionally rich in sugar, it being possible to obtain per hectare (2·47 acres) 13 tons of sugar and, by fermenting the milky mass of the seeds (which contain 20 per cent. of fermentable matter), about 2000 litres of alcohol, the residual cake having a high nutritive value.

(7) **Alcohol from Calcium Carbide (Synthetic Alcohol).** From the ethylene present in illuminating gas and in oil-gas, Hennel, a collaborator with Faraday, obtained (1825–1828) ethylsulphuric acid (sulphovinic acid), which on decomposition yielded alcohol. Berthelot studied this reaction more in detail in 1855, and Fritzsche in 1897, and more thoroughly in 1912, established the conditions for obtaining the maximum yield of alcohol: $C_2H_4 + H_2SO_4 = C_2H_5O \cdot SO_3H$ and the latter $+ H_2O = C_2H_5{\cdot}OH + H_2SO_4$; 100 kilos of hot concentrated sulphuric acid absorb 14 kilos of ethylene, 18 kilos of 100 per cent. alcohol being obtainable. The ethylene may be derived from coal-gas or by reduction of acetylene by means of hydrogen. A very large quantity of acid (450 kilos per hectolitre of alcohol) must be put into circulation, and this is not all recovered, and, further, requires reconcentration. Acetylene may give alcohol also directly (Jay et Cie., Paris, Ger. Pat. 149,893, 1902) by treating it with hydrogen and ozonised oxygen at 20° to 55° and condensing the small amount of aldehyde formed with ammonia.

In 1907, Jonas, Desmonts, and Deglotigna (Fr. Pat. 360,180) proposed preparing alcohol by first dissolving acetylene in mercurous nitrate and then heating the mass to boiling; the precipitate decomposes, regenerating the mercury salt and evolving vapours of acetaldehyde, which are condensed and converted into alcohol by means of sodium amalgam (nascent hydrogen). Further, the Griesheim-Elektron Company and N. Grünstein (Ger. Pats. 250,356, 253,707, 261,589 and 267,260, 1910–1912, and Fr. Pat. 440,658) succeeded in preparing acetaldehyde in good yield by passing acetylene into a sulphuric acid solution of mercury nitrate kept at 15° to 25°, an atmosphere of acetylene being maintained at the surface, while superposed on the liquid is a solvent which dissolves the aldehyde as it forms and thus prevents it from polymerising; the same end may be attained by causing separation of the aldehyde by dissolving sodium sulphate in the mass or by occasional distillation of the aldehyde. Transformation of the aldehyde into acetic acid or alcohol appears to be easy and to give good yields.

Shortly before the outbreak of the European War the Lonza Company of Vallese (Switzerland) erected a works for the large scale manufacture of acetic acid and anhydride from acetylene by a process analogous to that of the Griesheim-Elektron Company; they attempted also to produce synthetic alcohol. Messrs. Dreyfus of Basle likewise succeeded in preparing acetic acid, acetic anhydride and alcohol from acetylene, and during the war built three large plants—in Italy, France, and England; these were, however, failures, and seem to be speculations on the part of unscrupulous bankers and business men. A painful and clamorous echo of this entanglement of more than £4,000,000 was heard in the House of Commons early in 1918.

Prior to the war, alcohol from grain cost about £14 per ton, whilst that from acetylene cost at least £22, 2000 kilos of calcium carbide and 500 cu. metres of hydrogen being required, without taking into account the sulphuric acid and catalyst lost, the coal, patent rights, and sinking fund for such colossal plant.

REFINING AND PURIFICATION OF SPIRIT. After the introduction of rational methods of fermentation with selected yeasts and of more perfect rectifying appliances, the quantity of *actual alcohol* was considerably increased and it was generally sufficiently pure for ordinary commercial purposes. When, however, it became recognised that the harmful effects of alcoholism are aggravated by the presence in commercial alcohols for liquors, etc., of even minimal quantities of aldehydes and amyl alcohol, recourse was sometimes had to a special *purification* or *refining* of rectified spirits in order to give them a slight ethereal odour, which is greatly valued. Of the many and varied substances suggested for the purification, mention need only be made of wood charcoal in lumps calcined and cooled out of contact with air and placed in batteries of tall iron cylinders through which the alcohol is passed; when the charcoal becomes inactive it is revivified by means of superheated steam at 600°. The charcoal has an oxidising, esterifying, and decolorising action, but it does not fix the amyl alcohol. Treatment with fatty oils (which retain the aldehydes) and subsequent distillation are also used, as also is addition of carbonates of the alkalis and alkaline earths. Treatment with oxidising agents—ozonised air, potassium permanganate or dichromate, nitric acid, chloride of lime, etc.—has the disadvantage of forming acetic acid and ethyl acetate. Consequently Naudin prefers reducing the aldehydes with nascent hydrogen formed in the liquid itself by means of a copper-zinc couple.

R. Pictet has devised a totally different process: owing to the variations (at different temperatures) of the maximum vapour pressure of volatile liquids, he ascertained that the vapours obtained from a mixture of water or other substances with alcohol are the richer in alcohol the lower the temperature to which the mixture is heated. He boils the mixture at 50° to 60° in a vacuum and then rectifies the vapours in a column at a temperature of — 30° or — 40°, obtained by means of a sulphur dioxide refrigerating machine. The apparatus is somewhat complex, but it yields a well-refined pure spirit.[1]

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[1] **Tests for the Purity of Alcohol.** The tests mentioned on p. 131 will detect traces of water in so-called *absolute* alcohol.

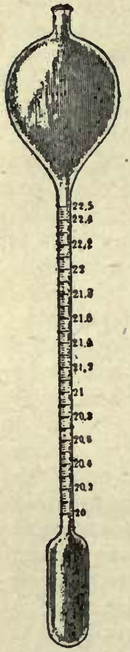

FIG. 144.

If alcohol is highly purified (*puriss.*), 10 c.c. of it, mixed with 1 c.c. of water and 1 c.c. of 0·1 per cent. potassium permanganate solution, should retain its red colour for twenty minutes, or for at least five minutes if the alcohol is termed *pure*; it should not become turbid on dilution with water, should give neither an acid nor an alkaline reaction (with phenolphthalein), and should remain unchanged with ammoniacal silver nitrate solution. To test for aldehyde the alcohol is diluted with water and a few drops distilled and tested by Rimini's reaction (*see* p. 131); or, for aldehydes in general, by Schiff's reagent (fuchsine solution decolorised with sulphur dioxide: 0·5 gram of fuchsine is dissolved in 500 c.c. of water and decolorised with 10 c.c. of sodium hydrogen sulphite solution of sp. gr. 1·26 and 10 c.c. of concentrated HCl); a few cubic centimetres of this reagent are coloured red when shaken with a few drops of alcohol containing traces of aldehydes.

Of more importance is the quantitative estimation of the *fusel oil* (*see* Note, p. 165).

Traces of *fusel oil* may be detected by Kamarowsky's reaction, *i. e.*, with salicylic aldehyde and sulphuric acid; H. Kreis's modification (1907) of this colorimetric reaction yields moderately accurate results. In the commercial control of the purity of alcohol use is generally made, for the quantitative estimation of the fusel oil, of Herzfeld and Windisch's modification of Röse's apparatus (Fig. 144); the method is based on the property possessed by chloroform of dissolving the higher alcohols and a very little ethyl alcohol, at the same time increasing in volume. The alcohol is first diluted very exactly to a concentration of 30 per cent. by volume, or, better, to the sp. gr. 0·9657 at 15·5° (*see* Table, p. 177; if the alcohol has a concentration, v, less than 30 per cent., then $\frac{10(30 - v)}{7}$ c.c. of absolute alcohol should be added). The Röse tube (washed with alkali, acid, water, alcohol, and ether and well dried) has a cylindrical expansion at the bottom containing 20 c.c. up to the first mark; then comes a tube 18 cm. long, holding 2·5 c.c. and graduated in 0·01 c.c.; at the top is a pear-shaped bulb of about 200 c.c. capacity, closed with a ground stopper. The tube is placed in water at 15° and into it are introduced by a long funnel reaching to the lower bulb 20 c.c. of pure chloroform at 15°, and then 100 c.c. of the alcohol diluted to 30 per cent. at 15° and 1 c.c. of sulphuric acid of sp. gr. 1·2857 (38 per cent. H_2SO_4). The tube is then closed, inverted so that all the liquid passes into the pear-shaped bulb, shaken vigorously for a minute (150 shakes) and placed erect in the water-bath at 15°, where it is left for fifteen minutes after a rotatory movement has been imparted to the liquid so as to collect the drops of chloroform adhering to the walls. The increased volume of the chloroform is then compared with that obtained in a similar test with pure alcohol of the same concentration. If no blank experiment is made, 1·64 c.c. is subtracted from the increase in volume as being due to the

ALCOHOL METERS OR MEASURES. These are important instruments, as in nearly all countries the manufacture of alcohol is subject to taxation which is calculated on the quantity of alcohol passing through a sealed meter indicating automatically the corresponding amount of pure alcohol (100 per cent.). The Siemens measurer is the one most commonly used (Figs. 145 and 146), and somewhat resembles the gas-meter (*see* p. 56) even in its registration. The alcohol, which enters laterally by the tube *l*, is discharged into the inner central part of the drum, *B*, *i. e.*, into *D*, this being divided longitudinally into three small chambers furnished with apertures, r^1, r^2, r^3; when the small

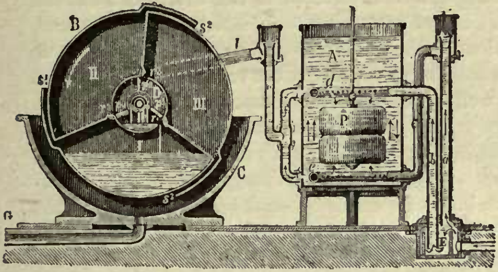

FIG. 145.

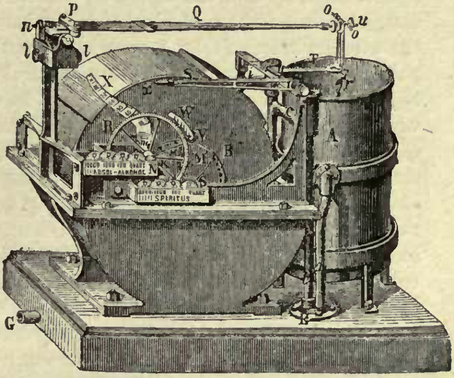

FIG. 146.

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ethyl alcohol dissolved. Each 0·01 c.c. increase in volume of the chloroform corresponds with 0·006634 per cent. by volume of fusel oil. For an alcohol rich in fusel oil which gave a final volume of chloroform of 22·14 c.c. the true increase in volume will be 22·14 — 1·64 — 20 = 0·5 c.c. The percentage, *f*, of fusel oil by volume on the original alcohol (not on that diluted to 30 per cent.) is calculated by the following formula :

$$f = \frac{(c - b)(100 + a)}{150},$$

where *c* is the uncorrected *increase* in volume of the chloroform, *b* is the correction, 1·64, due to the ethyl alcohol, and *a* indicates the number of cubic centimetres of water or absolute alcohol added to 100 c.c. of the original spirit to bring it to 30 per cent. *Example:* If 80 per cent. alcohol is used, 171·05 c.c. of water must be added to 100 c.c. to break it down to 30 per cent.; 100 c.c. of this then increases the volume of the chloroform from 20 to 21·94 c.c., so that :

$$f = \frac{(1{\cdot}94 - 1{\cdot}64)(100 + 171{\cdot}05)}{150} = 0{\cdot}54 \text{ per cent. by volume of fusel oil.}$$

The *furfural* is determined in 10 c.c. of distilled alcohol, to which are added 10 drops of colourless aniline and 2 c.c. of acetic acid; if a red coloration appears after twenty to thirty minutes furfural is present.

The estimation of small quantities of *benzene* in denaturated alcohol may be carried out by means of Röse's apparatus (for more than 1 per cent. of benzene). The best method is to dilute 100 c.c. of the alcohol to a concentration of 24·7 per cent. by weight and to distil the whole; the first 10 c.c. of the well-cooled distillate is diluted to 20 to 25 c.c. with water in a graduated cylinder; the volume of the benzene which separates is increased by 0·3 per cent., which is a constant error of the method. This method of Holde and Winterfeld (1908) is based on the fact that when the alcohol is diluted with water, the vapour pressure of the benzene is considerably augmented, whilst that of the alcohol is diminished.

To ascertain if *methyl alcohol* is present in alcohol, 1 c.c. of it is treated with 1 c.c. of chromic acid solution and 5 c.c. of water, the whole being then carefully distilled until only 0·5 c.c. remains. The distillate is condensed in a long, air-cooled tube and collected in a test-tube, the condenser-tube being washed out with 2 c.c. of distilled water. One drop of ferric chloride and two of albumin solution are added to the test-tube, which is shaken; 5 c.c. of concentrated sulphuric acid is then cautiously added. The immediate appearance of a violet ring at the zone separating the two layers indicates that the original alcohol contained more than 5 per cent. of methyl alcohol; if the coloration appears after a minute, the proportion is 1 to 5 per cent. and if after two minutes less than 1 per cent. (A. Vorisek, 1909). Another sensitive test is as follows : 1 c.c. of the spirit is shaken in a test-tube with 5 c.c. of 1 per cent. potassium permanganate solution and 0·2 c.c. (not more) of pure, concentrated sulphuric acid; after a rest of two to three minutes the liquid is shaken with 1 c.c. of 8 per cent. oxalic acid solution. When the mixture has assumed a brownish-yellow coloration, 1 c.c. of concentrated sulphuric acid is added, decolorisation then occurring in a few seconds. The liquid is then mixed with 5 c.c. of rosaniline bisulphite and allowed to stand : in presence of ethyl alcohol alone a greenish to intense violet coloration appears, this vanishing in a few minutes; with spirit containing as little as 1 per cent. of methyl alcohol the more or less pale violet colour persists for several hours.

chamber is about half full the alcohol falls into the large lower chamber (*e. g.*, *I*), which has a capacity of 4 litres. When this chamber is filled with alcohol the level of the latter reaches the chamber *D*, the alcohol then falling through r^2 into *II* and displacing the equilibrium, so that the drum, *B*, is forced round in the sense of the arrow. At the same time the first 4 litres of alcohol is discharged into the vessel *C*, which communicates with the storage reservoir by means of the tube *G*. The compartment *II* then occupies the position of *I*, and so on. The axis of the drum is connected with a suitable automatic registering device. At the same time, in the cylinder *A* in front of the drum, the alcohol which passes through raises the float, *P*, more or less according to its strength, and a screw, *Q*, operates the lever, *T*, and so moves the index, *S*, the point of which registers the alcoholic strength on a paper ribbon moving along a carefully calculated curve, *X*. In order that alcohols of different concentrations may be well mixed and so influence the float correctly, they are delivered at *E*, where there are two tubes; one of these, *a*, collecting the lighter alcohol, rises and then descends (*c*), discharging into the bottom of *A* by the perforated tube, *e*; the denser alcohol passes preferably along *b* and is discharged through the perforated tube, *d*, at the top of *A*, so that mixing is rapid and complete. The registration is also independent of the temperature of the alcohol, as its expansion (or contraction) is allowed for by that of the float.

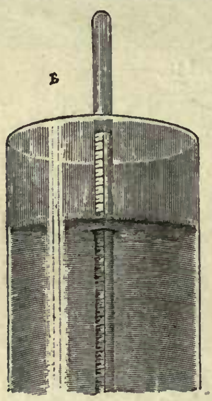

FIG. 147.

QUANTITATIVE ESTIMATION OF ALCOHOL AND ALCOHOLOMETRY. As a rule alcohol is sold by volume and not by weight; 1 litre of absolute alcohol weighs 0·7937 kilo or 1 kilo measures 1·2694 litres. Industrially alcohol is stated to be of so many *litre-degrees;* thus 100 litres of 2 per cent. alcohol would contain 200 litre-degrees (100 × 2), and 100 litres of 50 per cent. alcohol would indicate 5000 litre-degrees, which would also be given by 1000 litres of 5 per cent. alcohol; so also 75·48 litres of 100 per cent. alcohol would be expressed as 7548 litre-degrees. Alcohol is taxed on the basis of the number of litres of absolute alcohol.

The alcohol-content of an aqueous alcoholic solution is deduced from the specific gravity determined by the Westphal *balance*, or directly by the Gay-Lussac *alcoholometer* (at 15°) in France, or by the Tralles *official alcoholometer* (at 15·56°) in Italy and Germany, these giving the percentage of alcohol by volume contained in 100 vols. of the aqueous alcohol. The reading on the alcoholometer is made at the point of the stem coincident with the lower meniscus, which is well seen by looking rather below the surface of the liquid (Fig. 147); to avoid error, the alcoholometer must be so immersed that the whole of the graduated stem is not wetted (*see* Vol. I., p. 78). To determine the percentage by weight contained in 100 vols. the percentage by volume is multiplied by 0·7939 (specific gravity of absolute alcohol) and divided by the specific gravity of the alcohol examined (*see* Table on p. 175).

To correct the alcohol reading determined at a temperature different from 15° (or 15·56° for the Gay-Lussac alcoholometer), the following moderately exact formula of Francœur is used: $x = c \pm 0{\cdot}39t$, where x is the number of Gay-Lussac degrees at 15°, c the number of degrees found at the non-normal temperature, and t the number of degrees the latter is above or below 15°; the + sign of the formula is used if the temperature is below 15° and the − sign if it is above 15°. Thus an alcohol showing 72° on the Gay-Lussac alcoholometer at a temperature of 28° would have: $x = 72 - 0{\cdot}39 \times 13 = 66{\cdot}93°$ Gay-Lussac at 15°.

With dilute alcoholic liquids of complex composition (wine, beer, spirits, etc.) the alcoholic degrees cannot be deduced from the specific gravities. If, however, a given volume, *e. g.*, 100 c.c., is taken and distilled in the usual way (p. 2) or in the Salleron apparatus (Fig. 149) until all the alcohol has passed over (about 70 c.c.), the distillate may be made up to the original volume with distilled water and its specific gravity and alcoholic strength determined in the usual manner. In order to prevent frothing during the distillation of beer and wine a piece of tannin or a few drops of oil are added.[1]

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[1] The original type of the Salleron apparatus used by small wine merchants is that shown in Fig. 149.

In some cases the alcohol of wines and other liquors is determined by the Geissler *vaporimeter*, which indicates the pressure of the vapours from the liquid heated at 100°. By means

WINDISCH'S TABLE FOR CALCULATING THE STRENGTH OF AQUEOUS ALCOHOL SOLUTIONS

Sp. gr. at 15° C.	Grams of alcohol in 100 grms.	C.c. of alcohol in 100 c.c.	Grams of alcohol in 100 c.c.	Sp. gr. at 15° C.	Grams of alcohol in 100 grms.	C.c. of alcohol in 100 c.c.	Grams of alcohol in 100 c.c.
0·9999	0·05	0·07	0·05	0·9550	31·66	38·06	30·21
0·9992	0·42	0·53	0·42	0·9535	32·55	39·07	31·01
0·9985	0·80	1·00	0·80	0·9520	33·42	40·06	31·79
0·9978	1·17	1·48	1·17	0·9505	34·28	41·02	32·55
0·9970	1·61	2·02	1·60	0·9490	35·11	41·95	33·30
0·9963	2·00	2·51	1·99	0·9470	36·21	43·17	34·26
0·9956	2·39	3·00	2·38	0·9455	37·01	44·06	34·96
0·9949	2·79	3·49	2·77	0·9440	37·80	44·93	35·66
0·9942	3·19	4·00	3·17	0·9420	38·84	46·07	36·56
0·9935	3·60	4·51	3·58	0·9405	39·61	46·90	37·22
0·9928	4·02	5·03	3·99	0·9385	40·62	47·99	38·09
0·9922	4·39	5·48	4·35	0·9365	41·61	49·06	38·93
0·9915	4·81	6·01	4·77	0·9345	42·59	50·11	39·76
0·9909	5·19	6·47	5·14	0·9330	43·31	50·88	40·38
0·9902	5·63	7·02	5·57	0·9305	44·51	52·14	41·38
0·9896	6·02	7·50	5·95	0·9290	45·22	52·89	41·97
0·9889	6·48	8·07	6·40	0·9265	46·39	54·12	42·95
0·9884	6·81	8·48	6·73	0·9245	47·32	55·08	43·71
0·9877	7·29	9·06	7·19	0·9225	48·24	56·03	44·47
0·9872	7·63	9·48	7·53	0·9205	49·16	56·97	45·21
0·9866	8·05	10·00	7·94	0·9180	50·29	58·13	46·13
0·9860	8·48	10·52	8·35	0·9160	51·20	59·05	46·86
0·9854	8·91	11·05	8·77	0·9140	52·09	59·95	47·57
0·9849	9·28	11·50	9·13	0·9115	53·21	61·06	48·46
0·9843	9·72	12·05	9·56	0·9095	54·10	61·95	49·16
0·9838	10·10	12·50	9·92	0·9070	55·20	63·04	50·03
0·9832	10·55	13·06	10·36	0·9050	56·09	63·91	50·71
0·9827	10·94	13·53	10·74	0·9025	57·18	64·98	51·56
0·9822	11·33	14·01	11·12	0·9000	58·27	66·03	52·40
0·9817	11·72	14·48	11·49	0·8975	59·36	67·08	53·23
0·9811	12·20	15·07	11·96	0·8955	60·23	67·91	53·89
0·9807	12·52	15·46	12·27	0·8930	61·31	68·94	54·71
0·9801	13·00	16·04	12·73	0·8905	62·39	69·95	55·51
0·9796	13·41	16·54	13·13	0·8880	63·47	70·96	56·31
0·9791	13·82	17·04	13·52	0·8855	64·54	71·96	57·10
0·9786	14·23	17·54	13·92	0·8830	65·61	72·94	57·88
0·9781	14·65	18·04	14·31	0·8805	66·67	73·92	58·66
0·9776	15·06	18·54	14·71	0·8775	67·95	75·07	59·57
0·9771	15·48	19·04	15·11	0·8750	69·01	76·02	60·33
0·9766	15·90	19·55	15·51	0·8725	70·06	76·97	61·08
0·9761	16·32	20·05	15·91	0·8695	71·33	78·08	61·97
0·9756	16·73	20·55	16·31	0·8670	72·37	79·00	62·60
0·9751	17·15	21·06	16·71	0·8640	73·63	80·09	63·56
0·9747	17·49	21·46	17·03	0·8615	74·67	80·99	64·27
0·9741	17·98	22·06	17·50	0·8585	75·91	82·05	65·11
0·9736	18·40	22·55	17·90	0·8555	77·15	83·10	65·94
0·9731	18·81	23·05	18·29	0·8530	78·17	83·96	66·63
0·9726	19·22	23·54	18·68	0·8500	79·40	84·97	67·43
0·9721	19·63	24·02	19·07	0·8470	80·62	85·97	68·23
0·9716	20·04	24·51	19·45	0·8440	81·83	86·95	69·00
0·9710	20·52	25·08	19·91	0·8405	83·23	88·08	69·90
0·9705	20·92	25·56	20·28	0·8365	84·42	89·02	70·65
0·9695	21·71	26·50	21·03	0·8340	85·80	90·09	71·50
0·9685	22·49	27·42	21·76	0·8310	86·97	90·99	72·21
0·9675	23·25	28·32	22·47	0·8275	88·31	92·01	73·02
0·9665	24·00	29·20	23·17	0·8240	89·64	93·00	73·80
0·9655	24·73	30·06	23·86	0·8200	91·13	94·09	74·66
0·9645	25·45	30·91	24·53	0·8165	92·41	95·00	75·39
0·9630	26·51	32·14	25·50	0·8125	93·85	96·00	76·19
0·9620	27·19	32·93	26·13	0·8080	95·34	97·08	77·04
0·9605	28·19	34·10	27·06	0·8040	96·79	97·99	77·76
0·9590	29·17	35·22	27·95	0·7990	98·46	99·05	78·61
0·9580	29·81	35·95	28·53	0·7925	100·00	100·00	79·36
0·9565	30·74	37·02	29·38				

There are also Tables by Hehner, Haas, Tralles-Brix, Gay-Lussac, etc., which differ little (at most 0·1 to 0·2 per cent.) from that of Windisch.

For any specific gravity not given in the Table the corresponding alcoholic degree may be obtained easily and with sufficient accuracy by proportional interpolation.

USES AND DENATURATION OF ALCOHOL. The uses of alcohol are very varied, but are sometimes limited by the high price resulting from the taxation, which should be

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of a Table the alcoholic strength may be read off, knowing the vapour pressure; the latter is measured on a special barometric U-tube, *B* (Fig. 148), to one end of which is fixed the bottle, *O*, containing mercury and the alcoholic liquid and placed in the jacketed vessel, *D*, filled with steam from the boiler, *A*. This apparatus gives results which are influenced by several factors (dissolved carbon dioxide, salts, etc.), so that little use is made of it. In more general use is the *ebullioscope* devised in 1823 by Groningen and subsequently improved by Tabarié (1833), Brossard-Vidal (1842), Malligand (1874), Salleron (1880), and Amagat (1885). Malligand's form (Fig. 150) is the most commonly used, and is based on the different boiling-points possessed by alcoholic liquids of different concentrations. The reservoir, *F*, is provided with a cover, through which pass a thermometer, *T*, bent at a right-angle and a tube surrounded by the condenser, *R*. This cover is unscrewed and water poured into the reservoir as far as the lower mark inside, the cover being then screwed on (the bulb of the thermometer does not touch the water). The burner, *L*, is then lighted under the small chamber, *S*, which is traversed by a brass tube communicating with the reservoir; the part *a′* being rather higher than *a*, circulation of liquid takes place through the tubes and reservoir. When the mercury thread of the thermometer remains stationary owing to the water boiling and the steam hence having a constant temperature, the scale is adjusted by the screw, *E*, so that the zero-point corresponds with the end of the mercury column. The reservoir is then emptied, rinsed out with the wine, etc. (containing less than 15 per cent. of alcohol), and then filled with the wine to the upper mark, so that the thermometer bulb dips into the liquid when the cover is screwed on. The condenser is filled with cold water, the burner lighted, and the heating continued until the thermometer again shows a constant reading; the corresponding scale-reading then gives directly the percentage of alcohol by volume. In the case of sweet wines or beers it is advantageous to dilute with an equal volume of water, the result given by the instrument then being doubled.

An ingenious and simple *capillarimeter*, recently devised by Bosia and constructed by the

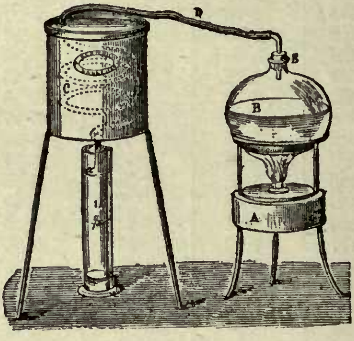

FIG. 149.

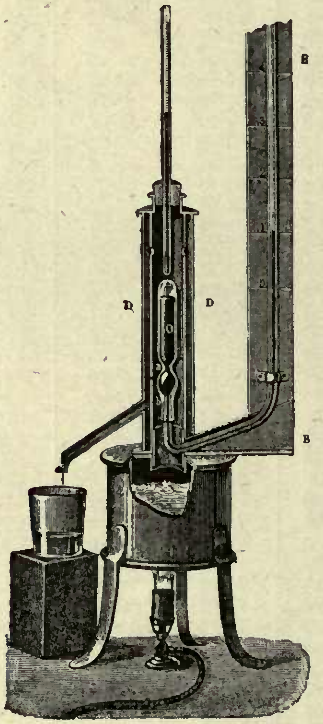

FIG. 148.

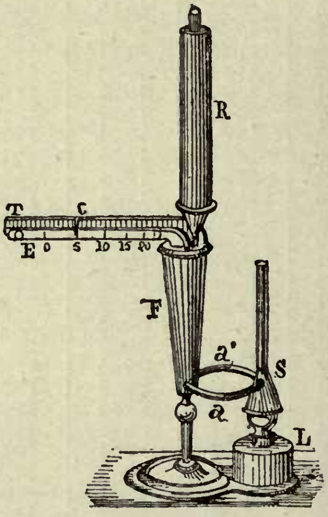

FIG. 150.

borne more especially by alcoholic beverages. In most countries alcohol for industrial purposes is almost free from taxation (*see later*), the use of such alcohol for drinking being prevented by addition of denaturing agents.

Since 1903 the manufacturing tax has been reduced in Italy to 12*s.* per hectolitre of 100 per cent. alcohol (denatured), the ordinary tax being £8 per hectolitre (a bonus of 25 per cent. or 40 per cent. is allowed if made from vinasse or wine). Denaturation was, however, allowed only for alcohol for making ether, collodion, mercury fulminate, varnishes, photographic papers or artificial silk, or for use as fuel or illuminant. In 1905, the tax of 12*s.* was abolished for denatured alcohol of any origin (cereals, vinasse, etc.), although the expense of denaturant remains, this amounting sometimes to 2*s.* 6*d.* or more for about 3 per cent. of the general denaturant (wood spirit, acetone, pyridine and benzene).

Denaturants vary in different countries [1] but are always substances which are coloured

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Italian Œnological Agency, Milan, gives the alcoholic strength of wines or spirits with sufficient accuracy in three or four minutes.

The following table indicates the volume of water to be added to 100 c.c. of alcohol of known strength in order to bring it to a definite lower concentration—

Concentration desired	Given Alcohol at									
	95 % by vol.	90 % by vol.	85 % by vol.	80 % by vol.	75 % by vol.	70 % by vol.	65 % by vol.	60 % by vol.	55 % by vol.	50 % by vol.
90%	6·4									
85	13·3	6·56								
80	20·9	13·79	6·83							
75	29·5	21·89	14·48	7·20						
70	39·1	31·10	23·14	15·35	7·64					
65	50·2	41·53	33·03	24·66	16·37	8·15				
60	63·0	53·65	44·48	35·44	26·47	17·58	8·76			
55	78·0	67·87	57·90	48·07	38·32	28·63	19·02	9·47		
50	95·9	84·71	73·90	73·04	52·43	41·73	31·25	20·47	10·35	
45	117·5	105·34	93·30	81·38	69·54	57·78	48·09	34·46	22·90	11·41
40	144·4	130·80	117·34	104·01	90·76	77·58	64·48	51·43	38·46	25·55
35	178·7	163·28	148·01	132·88	107·82	102·84	87·93	70·08	58·31	43·58
30	224·4	206·22	188·57	171·05	153·53	136·34	118·94	101·71	84·54	67·45
25	287·0	266·12	245·15	224·30	203·61	182·83	162·21	141·65	121·16	100·73
20	381·8	355·80	329·84	304·01	278·26	252·58	226·98	201·43	175·96	150·55
15	539·5	505·27	471·00	436·85	402·81	368·83	334·91	301·07	267·29	233·64
10	859·0	804·50	753·65	702·89	652·21	601·60	551·06	500·50	460·19	399·85

c.c. of water to be added to 100 c.c. of the more concentrated alcohol.

For example, if an alcohol of 90 per cent. by volume is to be diluted to 50 per cent. by volume, to 100 c.c. of the former must be added 84·71 c.c. of water.

This Table is calculated from the formula :

$$x = 100\left(\frac{S'x.v}{V'} - S\right)$$

where v is the strength of the more concentrated alcohol, S its specific gravity, S' and V' the specific gravity and alcoholic strength required, and x the quantity of water to be added to 100 c.c.

[1]

	Denaturants				
	Crude wood spirit	Crude pyridine	Acetone	Benzene	Crude benzine
	per cent.	per cent.	per cent.	per cent.	per cent.
France	7·5	—	2·5	—	0·5
Germany	1·5	0·5	0·5	—	—
,, (motors)	0·75	0·25	0·25	2·0	—
Austria	3·75	0·5	1·25	—	—
,, (motors)	0·5	traces	traces	2·5	—
Russia	10·0	0·5	5·0	—	—
Switzerland	5·0	0·32	2·2	—	—

In the United States methyl alcohol and pyridine are used, and, for special purposes, ether, cadmium iodide, ammonium iodide, etc.; denaturation has been allowed only since 1907.

In France denaturation costs about 9 fr. (7*s.*) plus a fixed tax of 2·2 fr. per hectolitre, and or of bad taste or smell and cannot be separated from the alcohol by any of the ordinary means (distillation, etc.), but which do not damage the alcohol for its industrial use. The denaturant should vary according to the use to which the spirit is to be put. There are hence in all countries a general denaturant (*see* preceding note) for alcohol as fuel, for motors, etc., and special denaturants. As colouring-matter, traces of crystal violet (hexamethyl-*p*-rosaniline hydrochloride) are used in Germany. Alcohol intended for the manufacture of ether, collodion, and artificial silk is denatured by the addition of ether and sometimes of a little acetone; in Italy, for varnishes, 2 per cent. of wood spirit, 2 per cent. of light acetone oils, and 20 per cent. of a 50 per cent. solution of sealing-wax are used. It has also been proposed to use part of the stinking products obtained on distilling certain bituminous shales (*see* p. 103).

The consumption of *denatured spirit* in different countries is as follows (thousands of hectolitres):

	1905–6	1908–9	1909–10	1910–11	1911–12	1912–13	1913–14	1914–15
Italy	36	91	95	112	109	124	143	121
France	550	630	656	676	681	724	—	—
United States	—	173	477	526	530	640	—	—
Austria	—	—	—	363	275	—	—	—
Germany	1400	1582	1883	—	1574	1720	—	—
Norway	—	—	—	0·4	—	—	—	—

The consumption of alcohol as a fuel for engines and for illuminating purposes is destined to increase rapidly in competition with petrol, which is continually rising in price (*see* p. 86). In all countries, more especially France and Germany, experiments have been made on the improvement of apparatus for the generation of light, motive power, and heat by means of alcohol or of suitable mixtures of alcohol with petrol or benzene.

Alcohol engines are still imperfect, and would give better results if the pressure could be increased, the distribution improved, and suitable arrangements devised for superheating and for starting. Existing petrol motors may, however, be worked with a mixture of alcohol, ether, and hydrocarbons in such proportions that they are mutually soluble.

Commercial benzene (85 per cent. benzene, 14 per cent. toluene, and 1 per cent. xylene) is highly soluble in 90 per cent. alcohol, and 60 vols. of petrol require 40 vols. of 95 per cent. alcohol for solution. Hence 95 per cent. alcohol must be prepared, 100 vols. of it dissolving 900 vols. of benzene and 150 vols. of petrol. If benzene were too dear (this will not be so for many years) use could be made of ether if its price were only 7 to 8 per cent. above that of alcohol; with ether, ordinary lamp oil would remain dissolved. A good mixture for engines, distinguished in France by the letters E.H.A., contains 65 per cent. of 95 per cent. alcohol, 10 per cent. of ether, and 25 per cent. of hydrocarbons (benzene and petrol; the latter facilitates evaporation of the alcohol at a low temperature and the ether aids in the starting of the cold engine) and has the calorific value 5850 cals. in comparison with over 10,000 for petrol.[1]

In the United States, de Keghel has prepared a carburetted alcohol by distilling 60 kilos of 93 per cent. alcohol in presence of 23 kilos of wood-tar or masut and 17 kilos of coal, with or without addition of small amounts of pyridine materials. The alcohol distilling over carries with it various hydrocarbons from the tar or masut and extracts others from the coal, 66 kilos of carburetted 90 per cent. greenish-yellow alcohol already denatured being obtained; this is redistilled after neutralisation with phosphoric acid.

In 1911, denatured 90 per cent. alcohol cost 46*s*. per quintal in Italy, whilst in Germany in 1909 it cost only about half this, namely, 25 marks (shillings) per hectolitre (after 1909,

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the Government makes a rebate of 9 fr. In Germany it costs only 2 marks (shillings), since much less, although sufficient, denaturant is added. In Italy denaturation is possibly excessive and too expensive.

[1] An automobile weighing 1200 kilos, on a journey of 174 kiloms. (109 miles) at 30 kiloms. (19 miles) per hour, consumed 11·3 litres of alcohol; under similar conditions, 10 litres of petrol are required. For an 8 h.p. car, 350 grams of alcohol or 500 of petrol are used per h.p. hour. For automobiles and explosion engines in general, the Paris Omnibus Company uses alcohol mixed with 50 per cent. of benzene, this giving a better thermal efficiency (34 per cent.). A domestic 25-candle lamp with an Auer mantle uses about 2·36 grams of alcohol per candle-hour. The use of *alcoholene*, a mixture of alcohol and ether, has now been proposed, and from a technical standpoint presents advantages over alcohol alone and also over other mixtures.

with the new tax, 48*s.*), in Austria 26*s.*, in Switzerland 24*s.* (retail), in Belgium 25*s.*, and in France 32*s.*[1]

STATISTICS AND FISCAL REGULATIONS. The alcohol industry owes its great development to the enormous use made of alcohol in numerous manufactures, and the chemical industries of a country in which relaxation of the ordinary fiscal duty does not render this possible are at a disadvantage compared with those of countries where alcohol, after denaturation, is procurable tax-free.

The production, importation, and exportation of alcohol in various countries are as follows (thousands of hectolitres, calculated anhydrous):

		1905–6	1908–9	1909–10	1910–11	1911–12	1912–13	1913–14	1914–15
Germany .	prod.	4,020	4,263	3,647	3,473	3,451	3,750	—	—
	exp.	194	10	12	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
Austria-Hungary	prod.	2,700	2,650	1,765	2,086	1,804	1,989	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
Russia .	prod.	4,500	—	—	—	—	5,580	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
United States	prod.	2,900	2,700	—	—	—	3,650	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
France .	prod.	2,700	2,428	2,392	2,182	2,987	2,596	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
Great Britain	prod.	1,284	—	1,500	—	—	—	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	15,300	—	—	—	—	—	—
Holland .	prod.	351	—	—	—	—	—	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
Belgium .	prod.	389	—	—	—	—	—	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	—	—	—	—	—	—	—
Sweden .	prod.	200	220	—	—	402	451	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	12	—	—	—	—	—	—
Norway .	prod.	43·7	—	—	11·3	—	—	—	—
	imp.	7·3	—	—	30·5	—	—	—	—
Italy . .	prod.	293	800[2]	419	297	260	349	372	398
	exp.	25	59	71	95	—	220	—	—
	imp.	—	—	—	—	—	—	—	—
Denmark .	prod.	154	—	—	155	—	—	—	—
	exp.	—	—	—	—	—	—	—	—
Switzerland .	prod.	—	—	—	54	57	53	—	—
	imp.	—	—	—	130	112	129	—	—
Turkey .	prod.	—	—	—	—	—	—	—	—
	exp.	—	—	—	—	—	—	—	—
	imp.	—	175	—	—	—	—	—	—
Bulgaria .	prod.	—	—	—	27	45	—	—	—
Whole world .	prod.	—	21,000	—	—	—	—	—	—

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[1] When, after the European War, the State monopoly of alcohol was mooted in Italy and France, the producers advised the respective Governments to lower the price of power alcohol to £1 per hectolitre so as to render advantageous its use on a large scale for motive power, lighting and heating, any loss being counterbalanced by an increase in the price of potable alcohol.

[2] This exceptional production corresponds with the famous cognac year (*see* Note, p. 181). The output was 80,000 hectolitres in 1878, 165,000 in 1888, and 187,000 in 1898–1899.

For every 100 litres of alcohol consumed as beverages the following amounts are used for industrial purposes: 54 litres in Germany, 19 in Austria, 18 in France, and 14 in Great Britain. These figures indicate the countries most addicted to alcoholism (*see* p. 184). The importation and exportation of alcohol for Italy are as follows (hectolitres):

		1905	1908	1910	1911	1913	1915	1917
Spirit in cask	imp.	2,508	822	641	647	624	133	9,853
	exp.	19,688	31,756	38,604	2,067	4,476	137,715	485
Cognac, casks and bottles	imp. about	1,330	1,460	1,500	1,200	1,175	265	690
	exp. „	940	300	4,250	1,420	715	5,600	170
Sweetened and spiced spirits, casks & bottles	imp. „	3,145	2,940	3,974	2,480	2,420	980	555
	exp. „	18,540	38,540	46,815	33,600	25,600	22,300	6,690

The alcohol produced in Italy is obtained from the following raw materials (the numbers represent hectolitres): [1]

	Cereals	Molasses	Beet	Wine	Vinasse	Fruit, etc.
Campaign of 1904–5	90,000	72,600	—	59,000	83,000	1,725
„ „ 1908–9	—	—	—	—	128,883	—
„ „ 1910–11	64,934	154,195	8,857	16,436	46,698	5,520
„ „ 1911–12	59,865	125,538	9,653	1,251	57,848	6,330
„ „ 1912–13	112,143	141,609	22,942	2,941	62,341	7,155
„ „ 1913–14	561,390	175,784	31,075	10,281	88,062	10,246
„ „ 1914–15	129,994	177,496	13,214	10,849	72,622	10,785

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[1] In 1913 there were in Italy 26 large distilleries using starchy substances, molasses, beet and dried grapes and 2673 using fruit, wine, vinasse, honey, etc. In 1904–1905 the spirit distilleries consumed 23,400 tons of maize, 600 of durra, and 1700 of barley, rye, millet and rice; also 28,000 tons of molasses and 5300 of other materials. To these must be added 575,000 hectolitres of wine, 260,000 tons of vinasse, and 1370 tons of fruit.

In 1908–1909, 368,000 tons of vinasse containing 3 to 4 per cent. of cream of tartar and about 4 per cent. of alcohol were treated; the mean production of vinasse is 800,000 tons.

In Italy there are three sugar works which also make alcohol (in 1911–1912 about 75,000 hectolitres of molasses) and one factory at Cavarzere (Venetia) which obtains alcohol directly from the beet (4000 hectolitres in 1911–1912). In 1911–1912 the distilleries of the Italian Distilling Company (at Milan, Savona, Padua, etc.) produced 25,000 hectolitres from cereals; the Corradini Distillery of Leghorn produced 10,000 hectolitres from cereals and the firm of Schiapparelli of Turin, 8000 hectolitres.

In the United States spirit distilleries consumed 1,270,000 tons of maize and about 100,000 tons of molasses (besides about 5000 tons of molasses for rum) in 1912.

In 1912–1913 there were in the United States 398 (in 1911–1912, 417) grain distilleries, 22 (18) molasses distilleries, and 450 (386) fruit distilleries, the materials used being 11,000,000 (12,000,000) hectolitres of grain giving almost 6,000,000 hectolitres of whisky, and 2,300,000 hectolitres of molasses giving 1,000,000 hectolitres of whisky. Further 130,000 hectolitres of molasses were used to make 103,000 hectolitres of rum, while 300,000 hectolitres of fruit spirit are also produced.

In Germany 80 per cent. of the alcohol comes from potatoes (the cultivation of which occupies 3,300,000 hectares out of a total cultivated area of 26,000,000 hectares). In 1911–1912 the output was 3,451,000 hectolitres of spirit, the materials used being: 1,856,626 tons of potatoes (2,520,000 tons in the previous year), 508,737 tons of grain, 49,100 tons of other starchy substances, 82,360 tons of molasses, 193,701 tons of beer residues, 336,000 tons of fruit, 324,000 tons of wine and vinasse, and 35,600 tons of yeast and fermentation residues.

In 1912, 150,000 hectolitres of alcohol were used in Germany to manufacture vinegar, 3300 for lead acetate, 36,500 for celluloid, 5500 for pegamoid, 32,500 for esters, 2100 for photographic gelatine, 8350 for dyestuffs, 225 for chloroform, 208 for iodoform, 4200 for coloured lacquers and 32,000 for other lacquers, 2650 for solid soaps, etc., and 5641 for scientific purposes.

In Hungary 1,000,000 hectolitres of alcohol were consumed in 1910, the distilleries employing 4500 workpeople.

In Austria 60 per cent. of the alcohol made is obtained from potatoes, about one-half of the Austrian output being furnished by Galicia, where there were 900 distilleries in 1911. In 1912 about 29,000 hectolitres of alcohol were converted into vinegar.

In France alcohol was protected by a Customs' duty of £2 16*s*. per hectolitre before the

In Italy the tax for manufacturing alcohol was 21*s.* per hectolitre at 100 per cent. in 1871, £4 in 1883, £6 in 1885, and £7 4*s.* in 1887; to this the sale-tax of £2 8*s.* was added in 1888 (so that the consumer paid about 23 pence per litre in taxation alone!); the sale-tax was abolished in 1904. A rebate of 90 per cent. of the tax is made on exported alcohol (added to marsala, vermouth, etc.). In 1903 alcohol obtained by distilling wine and vinasse and destined for industrial use was exempted of all taxation, and to alleviate the crisis in the wine industry it was proposed, but in vain, to grant a substantial bounty to the distillers of wine and vinasse. In 1911 the tax was raised to £10 16*s.* per anhydrous hectolitre at 15·56°, in 1914 to £13 4*s.*, and in 1919 to £20.

In other countries also, modifications have been made during the past few years in the fiscal regulations regarding alcohol, for the purpose principally of increasing the revenue.[1]

European War. In 1910 the output of 2,182,074 hectolitres of industrial alcohol was obtained: 21·6 per cent. from cereals, 23·5 per cent. from molasses, and 54·9 per cent. directly from beet; 420,000 hectolitres of potable spirit were made from wine. In preceding years the quantities of alcohol (hectolitres) obtained from different materials were as follows:

	From starchy matters	From molasses	From beetroot	From wine	From cider	Total
1885 . .	567,768	728,523	465,451	23,240	20,908	1,864,514
1897 . .	484,637	734,819	798,484	83,719	26,579	2,208,140
1901 . .	269,074	1,006,933	578,628	330,966	115,220	2,437,964
1904 . .	380,710	626,722	992,149	88,509	—	2,181,362
1908 . .	362,500	448,000	1,260,000	468,000	—	about 2,600,000

In 1911 1,073,628 hectolitres of alcohol were obtained from beet and in 1912, owing to the smaller beet crop, 1,014,690; 510,400 hectolitres were made from molasses in 1911 and 465,123 in 1912.

In Russia 50 per cent. of the alcohol is derived from potatoes, which grow well under the soil and climatic conditions prevailing there; the mean starch content of Russian potatoes is 18 per cent., the limiting proportions being 11 per cent. and 22 per cent.

	Tax per hectolitre £	s.	Year	Revenue £
[1] France	8	16	1913	15,978,312
Germany	6	3	1912	10,145,612
Great Britain	28	8	1913	18,595,435
Austria-Hungary	3	15	1911	4,477,373
Belgium	16	0	1912	2,179,677
Italy	10	16	1911	1,658,080
Spain	2	4	1913	739,757
Netherlands	15	0	1911	3,299,664
Sweden	5	16	1913	1,288,992
Norway	13	6	1913	288,000
United States	9	16	1911	32,182,061
Switzerland	Monopoly		1912	289,965
Russia	Monopoly		1911	63,501,812 (net) 83,534,099 (gross)

In Italy the revenue from the alcohol tax has amounted to:

1906	1907	1908	1909	1910	1912	1914
£1,556,004	1,206,053	575,902	954,320	1,546,768	1,917,512	1,315,457

In Germany the manufacturing tax of ordinary non-denatured alcohol varied prior to 1909 from 64*s.* to 72*s.* per hectolitre, this being entirely repaid on exported alcohol, which in certain cases also enjoyed a bounty of 9*s.* Before 1909 the tax was based on the volume of the wort, so that all distillers tried to work with concentrated worts (up to 25° Brix). Nowadays the payment is made on the volume of anhydrous alcohol produced, and the tax varies according to the production, which is established every ten years for each factory (*contingent production*). On this *contingent* quantity the tax is 105 marks (shillings) per anhydrous hectolitre, excess production paying 125 marks. There are then supplementary taxes of 4 to 14 marks to protect the small factories, so that a hectolitre of alcohol, costing of itself 28*s.* to 32*s.*, costs, with taxes, £7 4*s.* to £8 8*s.* The German Government received about £8,000,000 in alcohol taxes in 1908–1909 and expect in the future to raise this to £14,000,000. The increase in the tax for military expenditure was opposed by the socialists and clerical party with abstinence propaganda, and the consumption of alcohol fell in 1909–1910 by over 600,000 hectolitres. After 1909 the tax amounted to about 37*s.* for ordinary, and 19*s.* for denatured, spirit, and was increased still further later; as a result

UTILISATION OF DISTILLERY RESIDUES. All the components of the prime materials used in the production of alcohol are found (excepting the carbohydrates : starch and sugar) in the residues (grains, spent wash) left after the distillation of the alcohol.

These residues formerly formed inconvenient refuse (1 ton of grain gives 60 hectolitres of residues), since they readily undergo putrefaction and, if discharged into rivers or canals, contaminate the water. In exceptional cases, when the distilleries are in large agricultural centres, the residues are used in the wet state for cattle-food, but more commonly they are evaporated and dried, these dried grains being highly valued as a concentrated fodder, rich in proteins [1] and having a restricted (1 : 3 to 1 : 5) *nutritive ratio* (ratio between nitrogenous and non-nitrogenous substances).[2] In the fresh residues two-thirds of the part which is not water is dissolved and the remaining third suspended in the water. Potatoes give about 10 per cent. of dried residue, malt about 40 per cent., and maize 45 to 50 per cent.

It will hence be understood how distilleries have greatly increased the raising of cattle and consequently production of stable manure, thus contributing to the fertilisation of lands formerly unfertile.

The economics of the drying of these residues has always constituted a difficult problem owing to the presence of more than 90 per cent. of water in which part of the nutritive products is dissolved and to the fact that the dried residues sell at £4 to £5 10*s.* per ton. In many cases the liquid portion is abandoned and the solid part separated by filter-presses or centrifuges, but if the liquid part cannot be got rid of, even after addition of lime, ferrous sulphate, etc., it is best to evaporate it by means of the hot fumes from the flues, the operation being hastened with disc-stirrers of large surface and with fans. The evaporation is sometimes carried out in a vacuum apparatus (*see* Sugar) furnished with stirrers, by which means a marked economy in fuel is effected (*see also* Vol. I., pp. 563 and 568).

Of the various drying systems (Hatschek, Meeus, Porion and Méhay, Venuleth and Ellenberg, Theisen, Büttner and Meyer, etc.), we shall deal only with that of Donard and Boulet, which has been applied with advantage in France and recently also in Italy.

The solid residue from the filters or centrifuges (perhaps mixed with the evaporated residue of the liquid portion), still containing more than 50 per cent. of water, is carried by mechanical transporters into the vacuum drying apparatus (Fig. 151), consisting of a horizontal cast-iron cylinder rotatable about a hollow axis through which the steam enters or issues; its length and diameter are 2·5 metres. Inside are a number of tubes (heating area about 60 sq. metres) into which steam is passed from *D*, the condensed water being discharged without coming into contact with the mass to be dried. At the

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the consumption of industrial spirit, which had risen from 0·32 litre to 2·3 litres per head, diminished in 1912 to 1·3 litres per head per annum, while that of spirits fell from 6·2 litres to 3 litres in 1912. Potato spirit is made in 6400 large factories, that from cereals in 730 large and 6600 small factories, that from molasses in 27 special distilleries, and that from wine, fruit, and yeast in about 60,000 small distilleries. In Germany, besides the concession of untaxed denatured alcohol to all industries, non-denatured alcohol is also allowed free of tax to *scientific laboratories* and for medicinal uses and military explosives. The alcohol of spirituous beverages imported into Germany pays a Customs' tax of about £14 16*s.* per quintal. In Great Britain the spirit duty amounted to about £30,000,000 in 1907.

In France alcohol for drinking pays a tax of £10 per hectolitre, whilst industrial spirit is untaxed (as in Germany), and is sold at about 4·5 pence per litre.

[1] AVERAGE PERCENTAGE COMPOSITIONS OF THE PRINCIPAL RESIDUES

	Beetroot		Potato		Rye		Maize		Durra		Barley	
	Liquid	Dried	Liquid	Dried	Liquid	Dried	Liquid	Dried	Liquid	Dried	Liquid	Dried
Water . . .	91·0	10–12	94·0	8–10	91·0	10–12	90·6	10–12	90.3	10–12	75·0	14·0
Proteins . . .	0·9	6–7	1·3	18–24	1·9	22–28	2·0	24–26	2·0	24–26	4·0	20·0
Non-nitrogenous matter	7·2	60–65	2·6	45–55	5·2	48–52	4·9	35–40	5·1	30–34	10·0	46·0
Fatty matter . .	—	1·3–1·6	0·2	3–4	0·3	5–6	1·0	12–16	0·7	12–14	1·7	7·0
Cellulose	0·9	13–15	0·9	9–11	1·0	5–7	1·0	10–12	1·1	14–16	5·0	16·0
Ash		10–12	0·5	1–2	0·6	4–6	0·5	5–6	0·8	7–8	1·3	5·0

[2] For *fodder*, the *nutritive values* of the proteins, fats, and digestible non-nitrogenous substances are in the proportions 3 : 2 : 1, so that the *commercial value of a fodder*, expressed in *nutritive units*, is given by : nitrogenous substances × 3 + fatty substances × 2 + non-nitrogenous substances, given by the percentage composition of the *digestible* components.

other end, by means of the perforated axis, *G′*, the interior of the cylinder communicates with a double-action exhaust pump to carry away the vapour from the grains which are heated in a vacuum of 700 mm., while the cylinder slowly rotates (three turns per minute). The charge consists of 2½ to 3 tons of solid grains, which are dried (to 15 per cent. moisture, it then keeping well) in less than four hours, the coal consumption being about 150 kilos. By thus drying at a relatively low temperature (in a vacuum) and out of contact with air, the oil of the grains does not become rancid.

Since maize-grains contain as much as 15 to 18 per cent. of fat, it is sometimes convenient to extract them in one of the forms of apparatus described in the section on Fats.

Special interest attaches to the residues from **Molasses and Beet,** since these contain special nitrogenous compounds (amino-acids) and a large proportion of potassium salts utilisable for fertilisers or for chemical products. The evaporation of the liquid part of these residues may be carried to a certain stage (11° Bé. in the hot or 14° in the cold) in the ordinary vacuum plant, the mass being subsequently completely evaporated and the residue calcined in suitable furnaces (Porion model in France and Belgium) which are similar to the reverberatory furnaces or muffles used in the preparation of sodium sulphate (*see* Vol. I., p. 174). Care must be taken not to fuse the mass, which, when discharged, should still be carbonaceous and, indeed, sufficiently so to cause it to burn when placed in heaps outside the furnaces; the greyish or blackish mass thus obtained is known in France as *salin* (*see* Vol. I., p. 545; process for recovering pure potassium carbonate).[1]

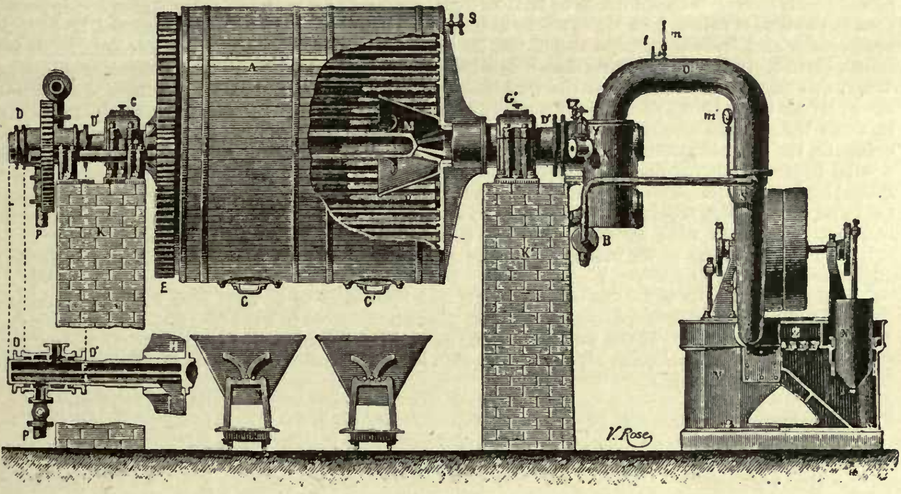

FIG. 151.

By this treatment, however, all the nitrogen compounds are lost, but in some cases these are used for the extraction of methyl chloride (*see* p. 116).

During recent years the utilisation of these nitrogenous substances has assumed great importance: according to the Effront patents (1907), the amino-acids are utilised by enzymic processes [2] for the preparation of organic acids and ammonium sulphate (with

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[1] A sample from an Italian distillery showed the following percentage composition: water, 11; insoluble matter (carbon, sand, etc.), 10; K_2SO_4, 9·5; KCl, 18; K_2CO_3, 43·7; Na_2CO_3, 6·5; potassium phosphate, 0·5.

[2] Ehrlich was the first to show that the fermentation of amino-acids is produced by *amidases.* Effront (1908) found that amidases occur especially in top beer-yeasts and in aerobic yeasts which, in seventy-two hours at 40° are able to transform, *e. g.*, all the nitrogen of an alkaline asparagine (*see this*) solution, and almost all the nitrogen of the yeast itself into ammoniacal nitrogen, organic acids being formed at the same time. Use is made more especially of butyric bacteria (or those often occurring in the soil), which act in an alkaline medium. From 1911 to 1914 the Effront process was employed in the Nesle (Somme) works with satisfactory results. The hot wash from the spirit rectifying column is cooled in large vessels (900 hectolitres) to 40° to 45°, neutralised with lime or crude potash and given an alkalinity of 15 to 20 c.c. of normal caustic soda per litre; a little colophony (*see* note, p. 167) is added together with nutrient material for the bacteria, *e. g.*, 50 to 200 grams of aluminium sulphate and 10 to 50 grams of manganese and magnesium phosphates and chlorides per hectolitre. A pure 5 to 7 per cent.

each hectolitre of alcohol produced correspond 25 kilos of ammonium sulphate and 35 grams of organic acids, principally acetic, propionic, and butyric). Since 1902, the Dessau Sugar Refinery, and since 1904 the Ammonia Company of Hildesheim, have utilised the nitrogen compounds as potassium cyanide and ammonium sulphate. In 1907 the Ammonia Company utilised 60 per cent. of the nitrogen of the residues, producing potassium cyanide to the value of £80,000 and ammonium sulphate to the value of £20,000.

ALCOHOLIC BEVERAGES[1]

WINE. Only the liquid obtained by the spontaneous alcoholic fermentation of the must of fresh grapes, without any addition, should be called wine. The fermentation is spontaneous owing to the presence on the grapes of *Saccharomyces cerevisiæ.*

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culture of butyric acid bacteria, already acclimatised to the concentrated wash is then introduced and a current of air passed through the liquid for six to ten hours. Vigorous action then ensues with evolution of carbon dioxide and hydrogen, the whole of the organic nitrogen being transformed in three days into ammonia and various proportions of trimethylamine, acetic and propionic acids, considerable amounts of butyric acid, glycerol and tartaric, citric and succinic acids, etc., as potassium salts. The Nesle works obtains per hectolitre of 100 per cent. alcohol, 30 kilos of ammonium and trimethylamine sulphates, 30 kilos of fatty acids, 4 kilos of succinic acid, 2·5 kilos of malic, citric and tartaric acids, 2 to 4 kilos of glycerine, and 30 kilos of potassium sulphate. When this mixture is rendered distinctly alkaline and distilled, the trimethylamine and ammonia are evolved, these being passed over a mixture of ammonium and trimethylamine sulphates. In this way the gaseous ammonia displaces the trimethylamine from its sulphate, forming ammonium sulphate, the trimethylamine liberated being either fixed by passing it into water, or sent through a tube heated to 1000° and thus transformed into hydrocyanic acid (from which cyanides are made) and methane. The alkaline residue left in the distilling vessel is acidified with sulphuric acid and the volatile monobasic acids (acetic, butyric, etc.; the dibasic acids and the glycerol do not distil) together with water distilled off; to the distillate is added anhydrous aluminium sulphate to absorb the water (which cannot be separated by distillation), the insoluble acids thus separated being rectified.

In the Nesle works 600 kilos of acetic acid and 1000 kilos of butyric acid were produced per day in 1914. The glycerine, dibasic acids and potassium sulphate were recovered by evaporating the residue to dryness. These works were closed in 1914 owing to the nauseous odours emitted.

[1] The average annual consumption per head in litres of absolute alcohol in the form of different beverages is as follows :

	Beer	Wine	Spirits	Total
Germany	4·8	0·66	4·1	9·5
Austria-Hungary	1·7	2·1	5·1	8·9
France	1·3	17·5	3·5	22·3
Great Britain	8·3	0·2	2·3	10·8
Belgium	8·7	0·6	3·7	13·0
Denmark	2·6	—	7·0	9·6
Sweden	2·3	0·06	3·9	6·26
Russia	0·2	—	2·5	2·7
United States	3·4	0·28	2·7	6·38
Italy	0·1	12·0	2·0	14·1

In Sweden 27 litres of alcohol in the form of spirits were consumed per inhabitant in 1830. In Italy the consumption was 6·5 litres per head in 1874 and 10·23 litres in 1898. In Norway the consumption of spirits, which was 40,000 hectolitres in 1864, fell to 15,000 in 1910, but increased in 1911.

The abuse of alcoholic beverages is leading to the ruin and decadence of certain nations, since it is largely the cause of depopulation and produces actual decay of the human organism. Alcoholism produces a diminution in stature, as is shown by the increased numbers of those unfit for military service; it quickly leads to crime and folly, and renders the organism easily attackable by all kinds of disease, its effect being felt to the third generation.

Alcohol acts as a poison which first excites and exalts, then intoxicates and depresses the psychic faculty more or less permanently. The abuse of wine and spirits is the real cause of much intestinal catarrh and of certain visceral lesions, and sometimes leads to chronic nephritis, heart-injury, enlargement and inflammation of the liver, hepatic cirrhosis, cerebral apoplexy, progressive paralysis, and often to madness.

Among the industrial classes it is thought that alcohol warms, prevents cold, and gives greater strength during work, but this is a great error based on appearances. Almost as soon as it is swallowed, the alcohol of wine and spirits is absorbed by the blood by means of the capillaries and brought into contact with all parts of the organism; the nervous centres are then more or less paralysed, and the numerous capillaries under the skin dilate, since an increased amount of blood rushes to the skin itself. The drinker has, indeed, a red face, but the sensation of great heat is only superficial; if the surroundings are cold, the heat of the body is more easily dispersed.

In many districts the fermentation is carried out on rational lines, selected yeasts being employed to impart the taste and aroma of wines of definite types.

This explains why drunken men, sleeping on the roads in the winter, quickly die of cold. Nansen, the famous Polar explorer, withstood temperatures 52° below zero without using alcoholic liquors.

The International Congress on Industrial Diseases, held at Milan in 1906, declared that the use of alcohol "is unnecessary for the nourishment of the workman, and becomes harmful where the work is heavy or long. As regards useful effects in the food rations of the worker, alcohol may be advantageously replaced by sugar, coffee, and tea." Alcohol may diminish the using-up of fat in the organism and hence the consumption of proteins, but as a food it is very costly and of little effect. Those accustomed to wine and beer may use it in moderation, although these beverages are of no advantage to the organism; the use of spirits should be abolished and it should be made a crime to give spirits or even wine to children.

During the last few years *alcohol-free wines* have been prepared by crushing grapes from the best vineyards and subjecting the must to filtration and pasteurisation (heating to 60°) so as to render it clear and to prevent fermentation; the wine is then stored in hermetically sealed, sterilised bottles. These wines retain the taste and fragrance of the grape and have considerable nutritive value, since the sugar of the grape remains unchanged (15 to 20 per cent.).

Alcohol also has a harmful effect on the reproduction of man, this explaining the *slowness* or the absence of increase in population of nations consuming much alcohol; as in France, where £6,000,000 was spent in 1898 on so-called aperitives (absinthe, bitters, etc.) alone. In Great Britain £60,000,000 is spent annually on spirits, and even in Switzerland £6,000,000. In 1913 England alone spent £140,000,000 on alcoholic beverages, Scotland £16,000,000 and Ireland £14,000,000, the average being £3 12*s.* per inhabitant; the number of public-houses was 141,000 (1 for 330 persons). In the same year there were 364,400 police-court cases of drunkenness, 2802 men and 2074 women dying of alcoholism, which also caused 3605 suicides and 2488 attempted suicides. Drink causes the direct or indirect death of about 45,000 people annually in France, 40,000 in Germany, 50,000 in England, 20,000 in Belgium, and 100,000 in Russia. In Italy, L. Ferriani stated that 627 cases of death in 1904 were evidently due to acute alcoholism. Dr. Marambat affirms that in France 72 per cent. of the criminals and 70 per cent. of the individuals (121,688) appearing annually before the courts make excessive use of alcoholic liquors. In Germany, A. Baer found that 41·7 per cent. (13,706) of the prisoners (32,837) were addicted to drink; in Switzerland, it is 41 per cent., and in England, 33 per cent. of those sentenced at the Assizes. In Holland, four-fifths of the crime is attributed to alcohol, and in Sweden three-fourths. Similar figures to the above have been given for Italy. In various countries it has been found that 25 per cent. of the lunatics are excessive alcohol drinkers. In the Salpêtrière Hospital of Paris, 60 out of 83 babies afflicted with epilepsy had alcoholic parents. In Germany, 30,000 persons are attacked every year by alcoholic delirium and other cerebral disturbances due to abuse of alcohol.

Alcoholism in Germany was a national calamity as early as the fifteenth and sixteenth centuries, when to the enormous consumption of beer was added that of brandy and, later, of cereal and potato spirit. After the eighteenth century, when the production of cereal and potato spirit became a great industry, their consumption as beverages increased enormously. In 1905 the annual expenditure for alcoholic drinks amounted to 47*s.* per head, or £8 for every person over fifteen years old, making a total of £120,000,000 for the whole of Germany, or about £80,000,000 for the working classes, corresponding with 12 per cent. of their wages. Every year there are 200,000 cases of inebriety, and 75 per cent. of the crimes against the person are the result of drunkenness. The question of alcoholism is closely connected with the social problem, as it is especially among the working classes and the ignorant and ill-nourished that the victims are found.

Abstainers are less liable to illness and usually live longer, as is shown by the following statistics. The Tables of the Sceptre Life Association for eleven years (1884–1894) show that the mortality in the temperance section (abstainers) was 57 per cent., and that in the general section (non-abstainers) 81 per cent. In times of epidemics nine out of ten non-abstainers die and only two out of ten abstainers.

The introduction of the alcoholic tendency into Africa, as a result of colonisation, wrought such havoc among the natives that the International Congresses against Alcoholism held in Brussels in 1899 and 1906 adopted various prohibitive and fiscal measures to save the black race of Africa from the terrible plague. Many remedies for alcoholism have been proposed, but singly they are almost all inefficacious, though more useful if combined.

Increase of the price of drink and diminution of the number of shops have proved almost useless in France, Belgium, and England. In England, however, the latest increase in taxation has diminished by one-third the consumption of spirit; the amount of beer drunk has fallen from 31·4 to 25·8 litres per head per annum, whilst the consumption of tea and wine has increased. In the United States the enormous taxes on alcohol have not diminished the consumption of liquors. Sweden has obtained good results by making a State monopoly of alcoholic drinks, by granting licence to sell only to trustworthy persons, by giving them special facilities for, and large profits on, the sale of other beverages and of food, by abolishing profit on alcoholic drinks, and by making the licensees responsible for cases of drunkenness on their premises. This example has been partially followed in America and England, and many temperance associations have helped by opening establishments where good food and drink are obtainable at low prices, alcohol being banned. In the United States from 1920 onwards the manufacture of any alcoholic drink, including wine and beer, will be prohibited, so that the grapes (250,000 tons per annum) of the prolific Californian vineyards will be used to make alcohol-free wine, syrups, jams, etc. Another

Grape must has the sp. gr. 1·08 to 1·10 and contains 70 to 86 per cent. of water, 16 to 36 per cent. of sugar (glucose and levulose, which reduce Fehling's solution); 1 to 3 per cent. of cream of tartar, tartaric, malic, and tannic acids; 0·4 to 1 per cent. of colouring, aromatic, extractive, gummy, and protein substances, and mineral salts. If the musts have to be transported over long distances, either they are concentrated in a vacuum or by freezing, or the fermentation is interrupted for a time by filtering them. One ton of grapes gives 600 to 700 litres of must and 300 to 350 kilos of unpressed or 160 to 200 of pressed residue (marc).

By fermentation in open vats the sugar is transformed, more or less completely, in seven or eight days into alcohol, large quantities of carbon dioxide being developed and a little glycerol, succinic acid, etc., always being formed. With more than 25 per cent. of sugar, *sweet wines* are obtained, and with less, *dry wines*. Fermentation cannot yield more than 15 to 16 per cent. of alcohol, as with more than this proportion the yeast dies. After the principal fermentation, when the wine, without the marc, is placed in casks of chestnut or oak, a slow fermentation goes on, this ceasing in the winter; with increase in the alcohol-content and lowering of the temperature, the yeast and part of the tartar (slightly soluble in alcoholic liquids) are deposited. In the spring, the clear wine is decanted into clean (sulphured ?) casks, which are kept full. It may now be placed on the market, or it may be further matured by clarifying it in the cask (by shaking with albumin and a little tannin and allowing to stand) and by decanting and filtering it several times during the course of a year or more before placing in well-cleaned bottles; the latter are corked by machinery with paraffin-waxed corks. As time goes on, the wine acquires a pleasing aroma owing to esterification of small quantities of the alcohol, this process being hastened sometimes by *pasteurisation*, which consists in passing the wine rapidly through coils heated to about 60°; this treatment also arrests certain incipient diseases, which would otherwise end by spoiling the wine (acidity, etc.). Sparkling wines are obtained by saturating the cold wine with carbon dioxide during bottling or by bottling sweet wines, the fermentation of which continues slowly in the corked bottle; in the latter case, however, a deposit forms at the bottom of the bottle.

In order to obtain wines of constant type on a large scale, co-operative wineries have been recently instituted in France, these collecting the grapes or must from a whole district, mixing it and preventing it from fermenting by saturating it in the cold with sulphur dioxide (70 grams liquid SO_2 per hectolitre); in this way, not only the yeasts, but also the moulds, bacteria, and unpleasant odours are destroyed and the must can then be kept for months in closed vessels. When part of the must is to be converted into wine, it is heated at 50° to 60° in a vacuum by allowing it to pass down a kind of rectifying column (Barbet, Ger. Pat. 195,235, 1906), the sulphur dioxide thus removed being recovered; selected yeast or other wine rich in yeast is then added, the resulting wines being of uniform and improved character, although somewhat rich in sulphates. These desulphurated musts might well be used as *non-alcoholic* wines. There are also special yeasts capable of destroying SO_2 in the musts and of starting fermentation. In Italy much was said in favour of co-operation in 1909 and 1910, but no trial has been made on a large scale.

The proportions of the most important components of wine vary between wide limits, owing to variation of the vines, soil, climate, system of wine-making, and season (certain wines contain manganese, sometimes as much as 27 mgrms. per litre).

It is hence difficult to ascertain if there has been an artificial addition of constituents similar to those naturally present in the wine, so that considerable dilution with water and addition of alcohol, glycerol, tartar, sugar, etc., are not easy to detect if they do not exceed such limits. *Natural wines* may contain 8 to 16 per cent. of alcohol, 1·6 to 4 per cent. (for dry wines, and as much as 20 per cent. or more for sweet wines) of dry extract (obtained by evaporating a definite volume to dryness on a water-bath and drying in an oven at 100°), 0·5 to 1·5 per cent. of various acids and tartar (expressed as tartaric acid) and 0·15 to 0·45 per cent. of mineral substances (*ash*, obtained by calcining the dry extract); the glycerol

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effective factor against alcoholism is education and explanation of the evil effects of the habit: in schools, churches, barracks, the streets, workshops, books, reviews, newspapers, advertisements —indeed everywhere should an intelligent campaign be waged against alcoholic liquor which, as Gladstone said in the House of Commons, *commits more slaughter in our days than the three historic plagues: famine, pestilence, and war, since it decimates more than famine and pestilence and kills more than war, and is in all cases a disgrace often lowering man below the level of the brute.*

varies from one-seventh to one-fourteenth part of the alcohol. Naturally these variations are much smaller for wines of a certain quality and year and obtained from one and the same district, for which the results of numerous analyses have been collected.

In Italy the following *minimum* legal limits have been established as those which must be reached for a wine to be called natural (except in cases where *genuine* wines of the same origin and year are shown to give lower limits): alcohol, 8 per cent. by volume in white wines, 9 per cent. in red; dry extract without sugar, 1·6 (white), 2·1 (red); total acidity expressed as tartaric acid, 0·5 (white), 0·6 (red); ash, 0·15 (white), 0·2 (red); alkalinity of the ash (for nonplastered wines) in cubic centimetres of normal alkali per litre, 11 (white), 16 (red); the glycerol should be from one-seventh to one-fourteenth by weight of the alcohol, and the relation between ash and extract (for dry wines or for sweet wines after deducting the sugar) should be about 1 : 10; *plastering*,[1] expressed as sulphuric acid, should not exceed 0·2 per cent.

In France and now also in Italy, in deciding if a wine is watered, use is made of *Gautier's rule* (corrected), according to which the sum of the percentage of alcohol by volume and the total acidity (as sulphuric acid) per litre should reach the value 12·5 for red wines and 11·5 for white wines.

Use is sometimes made of Halphen's rule (1906–1913), the results of which are credited by some and discredited by others (Issoglio and Possetto, 1914; Astruc and Mahoux, 1908–1911; Prandi, 1914; Pratolongo, 1917; Scurti and Rolando, 1917; Galeazzi, 1916, etc.). According to this rule, the ratio (x) between the fixed acidity (expressed as sulphuric acid and increased by 0·7) and the percentage of alcohol by volume (y) should differ by not more than 0·120 from the theoretical value calculated from the expression $x = 1{\cdot}160 - 0{\cdot}07\ y$; thus, for a wine with 10·2 per cent. of alcohol and fixed acidity 3·88, $x = (3{\cdot}88 + 0{\cdot}7)/10{\cdot}2 = 0{\cdot}449$, while the theoretical value would be $1{\cdot}160 - (10{\cdot}2 \times 0{\cdot}07) = 0{\cdot}446$.

Wines weak in alcohol or tartar do not keep well in the warm weather. A weak wine may be improved by either mixing with stronger wines or concentrating by freezing, water then separating in the form of ice (this method, in use even in the Middle Ages, has recently been patented in Italy !).

New wine has sometimes the smell and taste of rotten eggs, *i. e.*, of hydrogen sulphide; this may be remedied by decanting it into casks in which sulphur has been burnt: $2H_2S + SO_2 = 2H_2O + 3S$.[2]

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[1] In order to prevent certain diseases to which southern wines low in acidity are liable, recourse is had to the addition of sulphites, or potassium metabisulphite (*see* Vol. I., p. 544), which increase the quantities of sulphuric acid and sulphates. Thus some wines remain clear in the bottle, but become turbid and dark on exposure to the air; this disease, termed *casse*, is prevented by addition of potassium metabisulphite, which also arrests secondary fermentation. To make certain weak wines keep better in summer in tapped casks, calcium sulphite is added, this giving a slow evolution of sulphur dioxide.

The keeping qualities of certain wines are improved by *plastering*, which consists in adding to the fermenting must a certain quantity of gypsum (calcium sulphate), but the total sulphates are restricted by law to 2 grams per litre (calculated as normal potassium sulphate), excessive proportions of sulphates being considered injurious to health. It was formerly thought that the gypsum with the cream of tartar would give rise to insoluble calcium bitartrate and acid potassium tartrate, but instead of the latter normal potassium sulphate is the more probably formed: $2C_4H_5O_6K + CaSO_4 = C_4H_4O_6Ca + C_4H_6O_6 + K_2SO_4$ (Magnanini and Ventura, 1902; Bussy and Buignet, 1865; Pollacci, 1878; Roos and Thomas, 1896; Manzato, 1896 and, especially, Bornträger, 1917 and 1918). Incipient sourness of wine may be corrected by adding normal potassium tartrate or, better, potassium carbonate in amount calculated on the quantity of volatile acids (acetic, etc.) present, and subsequently clarifying.

[2] To desulphur musts and wines use is sometimes made of a small quantity of *urotropine* (*hexamethylenetetramine*), which decomposes into ammonia and formaldehyde, the latter fixing the sulphur dioxide; such addition may be detected, according to Fonzes-Diacon and Bonis (1910), by distilling 25 c.c. of the wine with 3 drops of sulphuric acid, acidifying the first 5 c.c. of distillate with 1 c.c. of sulphuric acid, and observing if it colours a solution of fuchsine decolorised with sulphur dioxide. The residue from the distillation is rendered alkaline with magnesium hydroxide and distilled, the vapours distilling over being condensed in a known volume of N/10 sulphuric acid, which is titrated back to ascertain how much ammonia distils over from the urotropine.

Even in a dilution of 1 : 50,000, urotropine may be detected by addition of mercuric chloride, which forms a precipitate in the shape of many-rayed stars. With white wine the reaction is obtained directly after addition of a little hydrochloric acid; red wine is shaken first with solid lead acetate and then with sodium phosphate, and filtered, the filtrate being tested with $HgCl_2$. Milk is acidified with HCl, shaken with solid ammonium sulphate, filtered and, if turbid, shaken with petroleum ether, the reaction being then applied (Rosenthaler, 1913).

From the **vinasse** remaining after the wine is drawn off a little rather rougher wine may still be obtained by subjecting it to considerable pressure, and from the pressed vinasse alcohol (*see above*) and tartar (*see later*) may be extracted.

The testing or **analysis** of wine is usually limited to determining the alcohol (by the method described on p. 174), dry extract, ash (*see above*), glycerol, plastering, and total acidity, and to testing for the addition of colouring-matter and other adulterations. The complete analysis of wine is described in Villavecchia's "Applied Analytical Chemistry," Vol. II., pp. 175 *et seq.*

Statistics. The countries which produce the most wine are France, Italy, and Spain. For Italy the statistics are very contradictory, and even the official ones are erroneous; for instance, the production for 1909, which was given officially as 40,000,000 hectolitres, was officially corrected in 1910 to 60,000,000 hectolitres. In various countries the output has been greatly diminished owing to invasion by phylloxera.[1]

The average annual output of grapes in Italy in 1909–1916 was 6,400,000 tons; in 1912, 67,000,000 and in 1913 8,000,000 tons were produced.

Italy imports on an average 900,000 bottles of fine wines, of the value £100,000, per annum.[2]

In Milan in 1909 duty was paid on 1,000,000 hectolitres, the Corporation receiving £420,000, and the consumption per head being 200 litres.

In 1905 Italy exported to Germany 124,000 quintals of dessert grapes, whilst France exported only 78,000 quintals. In 1892 Italy exported about 260,000 hectolitres of wine to Germany, but less amounts in subsequent years.[3]

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[1] Phylloxera (*P. vastatrix* and *P. vitifolia*) is an insect allied to the aphides and about 1 mm. long. It lives on the roots, leaves and tendrils of the vine, and quickly kills the latter, the roots blackening and decomposing. It was introduced into Europe on vines imported from America. The French vineyards were devastated by it in the period 1876–1889 (*see above*: "Statistics"). the ordinary remedies (flooding, carbon disulphide, potassium trithiocarbonate, etc.; *see* Vol. I., pp. 495, 547) being without avail, owing to the violence of the attack. Almost all the French vines had to be destroyed and replaced by American phylloxera-resisting vines on which were grafted the French vines, these giving grapes of the original qualities. Hungary was also hit hard by phylloxera, the output of wine falling from 7,000,000 hectolitres in 1880 to 2,000,000 in 1902. In Italy phylloxera has spread alarmingly, the vineyard areas attacked being: 2458 hectares in 1879; 75,612 in 1889; 351,033 in 1899; 410,260 in 1909, and 605,305 in 1911.

[2] The output of wine in other countries is as follows (thousands of hectolitres):

	1902	1907	1908	1909	1910	1911	1912	1913	1914	1915
Germany	2,000	2,492	3,135	2,020	846	2,922	2,019	1,005	921	2,698
Austria	5,200	4,250	8,142	6,252	2,546	3,836	3,970	4,352	3,615	—
Hungary	2,000	3,792	8,023	4,364	2,764	4,939	—	—	—	—
Bulgaria	2,300	866	1,643	1,318	770	551	715	—	—	—
Spain	16,000	18,384	18,557	14,716	11,283	14,747	16,465	17,105	16,168	8,789
Greece	1,000	—	—	—	—	3,230	—	—	3,182	3,042
Portugal	5,000	—	6,869	—	—	4,074	—	—	—	4,910
Roumania	2,700	967	2,283	1,270	1,713	993	1,589	1,158	660	1,670
Russia	2,300	—	—	—	2,310	—	2,600	—	—	—
Serbia	500	536	856	394	153	—	—	—	—	—
Switzerland	—	681	925	408	408	854	903	264	507	870
Corsica	—	—	254	194·4	193·4	159	147	—	125	42
Algeria	—	7,853	7,803	8,228	8,414	8,833	—	—	—	—
Tunisia	—	357	345	350	250	440	290	300	200	125
Turkey & Cyprus	2,000	—	—	—	—	—	1,800	—	—	—
Argentine	1,500	2,843	3,350	3,900	3,817	4,085	5,000	5,144	4,823	4,515
Chile	2,500	1,893	2,260	2,227	1,331	1,964	2,262	2,943	3,080	1,614
Uruguay	—	185	162	170	147	105	194	165	165	114
Australia	327	202	250	209	266	226	277	214	—	—
United States	1,100	—	—	1,166 (tons of grapes)	—	—	—	—	—	—
Whole World	126,000	142,000	161,500	157,500	89,850	127,500	144,000	138,000	146,000	105,500

[3] The import duties levied by different countries on Italian wines before the war were as follows: Germany, 29*s*. per quintal; Belgium 18*s*. 6*d*.; Holland 34*s*.; Great Britain 23*s*. for wines with less than 14·84 per cent. of alcohol, and 54*s*. 6*d*. for stronger ones; Russia, 45*s*.; United States, 54*s*. 6*d*.; and British India, 33*s*. 6*d*.

The following figures represent hectolitres (1 hectolitre = 22 gallons):

	France	Italy	
	Production	Production	Exportation[1]
1875	83,000,000	28,000,000	363,000
1879	25,000,000 (phylloxera)	34,000,000	1,075,000
1887	24,333,000	34,000,000	3,603,000 (2,800,000 to France)
1889	23,000,000	22,000,000	1,440,000 (commercial treaty with France broken in 1887)
1893	59,000,000	32,000,000	2,362,000 (750,000 to Austria-Hungary; 300,000 to Switzerland,[2] and 426,000 to America)
1897	32,000,000	28,000,000	2,400,000
1901	58,000,000	44,000,000	1,334,000
1902	—	35,000,000	2,164,000 (976,300 to Austria-Hungary)
1904	—	42,000,000	1,200,000 (Austro-Hungarian market lost by new commercial treaty)
1905	57,000,000	28,000,000	980,000 (worth £1,400,000)
1908	66,500,000	52,000,000	1,200,000
1909	66,000,000	60,000,000	1,450,000 (France has a vine area of 1,625,630 and Italy of 3,500,000 hectares)
1910	28,723,000	29,293,000	1,812,000 (£2,400,000)
1911	53,879,156 (of which 8,900,000 in Algeria and 160,000 in Corsica)	42,655,000	960,722 (plus bottled wine to the value of £400,000)
1912	63,831,000	44,123,000	863,970 (£1,440,000)
1913	52,000,000 (with Algeria)	52,240,000	1,466,600 (£2,440,000, plus bottled wine worth £520,000)
1914	70,134,160 (with Algeria)	43,000,000	1,785,500
1915	25,000,800 (European war)	19,000,000	742,000
1916	44,800,000 (of which 8,800,000 in Algeria)	39,000,000	398,000 (£1,280,000)
1917	42,000,000 (with Algeria)	48,000,000	1,024,000 (£3,840,000)
1918	—	36,408,000	2,560,000 (£9,600,000, plus bottled wine worth £560,000)
1919	—	30,000,000	

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[1] The wine (hectolitres) exported from Italy to different countries is as follows:

	1909	1910	1911	1912	1913
France	43,725	73,560	45,446	23,679	235,578
Germany	193,960	93,868	85,130	19,022	46,640
Switzerland	922,950	637,300	332,415	200,565	569,465
Egypt	32,000	23,420	9,620	7,000	8,300
Argentine	211,620	241,900	165,977	153,720	148,954
Brazil	129,589	156,226	136,980	176,695	186,485
United States	138,180	126,522	70,200	73,320	99,224
Other countries	124,613	140,887	111,760	84,200	117,985

[2] The following is a statistical *résumé* of the wine imported into Switzerland (hectolitres):

From	1906	1908	1910	1912	1913	1914
Italy	137,843	531,776	828,559	200,000	570,000	693,000
France	273,731	363,769	216,909	—	—	—
Spain	123,587	415,052	422,775	—	—	—
Austria	53,411	69,634	110,608	—	—	—
Greece	9,370	12,209	64,874	—	—	—

Among the many taxes imposed by Italy to settle the enormous war debts was one (dated September 30, 1919) of 9*s.* 6*d.* per hectolitre on wine produced and on that remaining from 1918.

MARSALA. This is a liqueur wine made for the first time at Trapani in 1773 by J. Woadhouse of Liverpool to compete with the world-famous Madeira. In 1812 another large establishment was started by the Englishman, Benjamin Ingham, and in 1840 Vincenzo Florio's factory, which has since become the most celebrated. The prime material for the manufacture of Marsala is white Trapani wine with 13 per cent. of alcohol, to which is added (in quantity varying for different types of Marsala) the must (*cotto*) of very mature white grapes, concentrated in open boilers until two-thirds has evaporated; then is added, in varying amount, *sifone*, obtained by filling a cask to the extent of three-fourths with clear must from a very ripe white grape, and one-fourth with pure alcohol (free from tax if for export), mixing and allowing to age so as to develop the Marsala aroma.

Mixtures of these three components in different proportions give the various brands of Marsala: the *Italian brand* is the least alcoholic (16 to 17 per cent.), the *original English brand* the strongest (up to 24 per cent. of alcohol), while the *Margherita* and *Garibaldi brands* are of intermediate strengths and are sweeter.

In 1905 Italy exported in cask 29,765 hectolitres of Marsala, worth £83,280, and 51,000 bottles, value £2040; in 1908, 24,900 hectolitres; in 1910, 32,500; in 1912, 30,381 and in 1913, 28,695 hectolitres (£103,302) in cask and 3000 (£19,200) in bottle.

VERMOUTH. This was prepared formerly in Tuscany, but nowadays almost exclusively in Piedmont, where the industry was started in 1835 by Giuseppe Cora and A. Marendazzo.

The prime material for manufacturing vermouth is the muscat wine of Asti and of the Monferrato heights, which contains 6 to 11 per cent. of alcohol and 2 to 4 per cent. of sugar; with this is mixed 2 to 5 per cent. of a vinous infusion of aromatic drugs, in which wormwood predominates, and which contains also sweet flag, juniper, gentian, etc.; finally alcohol is added to bring the strength up to 15 to 18 per cent. and sugar to the density of 5° to 9° Bé. (if for exportation, 90 per cent. of the alcohol and sugar taxes are refunded). Sparkling vermouth is made by saturating it with CO_2 in the cold under pressure.

It cannot be said that in the manufacture of Marsala and vermouth all the rational methods prescribed by modern œnotechnics are followed.[1]

The production of vermouth in Piedmont is now about 300,000 hectolitres, the exports (especially to America) being 8960 hectolitres in cask and 64,980 in bottle in 1906; 7874 in cask and 83,300 in bottle in 1908; 10,176 (£27,680) in cask and 100,000 (£464,920) in bottle in 1909; 20,400 (£53,040) in cask and 173,760 (£760,000) in bottle in 1910; 25,000 in cask and 94,000 in bottle in 1911; 32,000 in cask and 131,500 in bottle in 1912, and 34,300 (£119,360) in cask and 133,600 (£720,000) in bottle in 1913.

CIDER. This is an alcoholic drink obtained by the partial fermentation of the juice of apples and pears (perry). It is largely used in the north of France, in Germany, and in Switzerland. It is consumed almost immediately it is made. In France the production varies from 8,000,000 to 30,000,000 hectolitres, part of which is distilled to produce alcohol (30,000 to 70,000 hectolitres of alcohol).

LIQUEURS. These contain 40 to 70 per cent. of alcohol. The finest are those obtained by collecting the first, more highly alcoholic distillate from other fermented liquors. Such are **brandy** (prepared by distilling vinasse or wine and containing 45 to 55 per cent. of alcohol), **cognac, kirschwasser** (obtained especially from the cherries of the Black Forest), *rum* (prepared principally in Jamaica by distilling fermented cane-sugar molasses), *maraschino* (prepared from small Zara cherries), *gin* (from juniper berries), *atole* or *chica* of South America, *arrack* of the Arabs and Indians (prepared from rice, cane-sugar, and coconuts), *schnapps* of the Germans (potato spirit), etc.

The other class of liqueurs comprises those obtained from aromatic substances, sugar, and more or less concentrated pure alcohol. In this way are obtained *rosoli, anisette, absinthe* (alcoholic decoction and distillation with wormwood)—much used in France and the principal cause of the terrible effects of *alcoholism* (p. 184)—*crème de menthe, crème de café*, etc.; *ratafia* from fruit must, spirit, and sugar; *Chartreuse* (the most celebrated

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[1] In Italy and also in other countries vermouth may not be coloured with aniline dyes, but the Municipal Hygiene Authority of Milan limits such prohibition to vermouth wine, colouring being allowed if the product is declared simply as vermouth (as with liqueurs).

was that prepared by the Carthusian monks, before their expulsion from France in 1904, from balm-mint, cinnamon, saffron, hyssop, angelica, sugar, alcohol, and other ingredients), *coca* (from Bologna), *curaçao* (first prepared from two kinds of orange in the island of Curaçao in the Antilles), *kummel* (in Russia the best kinds are obtained by distilling brandy or alcoholic liquids with Dutch cumin seeds and dissolving pure sugar in the highly alcoholic distillate). It is unnecessary to mention that all liqueurs, even the most celebrated, are more or less poorly imitated in all countries with mixtures in no way resembling the original types, but the latter always command very high prices.

Cognac is a brandy prepared especially in Charente by very carefully distilling weak wines of special vintages and refining and maturing the product in casks of Angoulême or Limousin oak, which gradually imparts to the spirit a pale yellow colour and a characteristic aroma. The finer and older brands sell at as much as £40 per hectolitre (*see* note, p. 180).

FERMENTED MILK. This bears the following names according to the locality and method of its preparation and the nature of the milk from which it is made: *kephir, koumis, galazin, leben* (Egypt), and *mazun*. The first three of these are the best known.

KEPHIR, or Kefir, is of very ancient origin among the Caucasian highlanders, who nowadays make enormous use of it and jealously keep the secret of its preparation. There is a legend to the effect that Allah was the first to make it, and that he recommended it as a remedy for various diseases. Kephir is simply cows' milk (fresh or skim) fermented by the addition of a special ferment in the form of granules, which the Russians call "*fungi*" and the Tartars "grain or millet of the Prophet," as they regard it as discovered by Mahomet. It was only in 1882 that Dr. Dmitrieff called the attention of the rest of Russia and of Europe to kephir and its great recuperative properties in cases of lung diseases.

Kern and, later, Freudenreich showed that the alcoholic fermentation of milk with *millet of the Prophet* is due to the simultaneous action (*symbiosis*) of the new *Saccharomyces kephiri* (similar to ordinary *Saccharomyces ellipsoideus*), a *streptococcus*, and a *bacillus*. The alcoholic fermentation of milk-sugar with evolution of CO_2 takes place rapidly and is always accompanied and followed by acid fermentation (lactic acid), which partially dissolves the casein (propeptones) and forms a very fine coagulation, almost a frothy emulsion. In practice the kephir *granules* (or about 2 grams of kephir-extract per litre of milk) are softened with tepid water (30° to 35°) for a couple of hours, the milk being then added and the mixture shaken every hour for eight hours; it is then sealed in clean bottles fitted with mechanical stoppers and is shaken now and then, the temperature being maintained at 15° to 20°; in twenty-four hours' time the kephir is ready; it forms a slightly alcoholic and acidulated dense, frothing liquid. If the kephir is left in closed bottles for two days, the pressure increases and the mass becomes more acid and more liquid; by the third day it becomes extremely acid and contains up to about 2 per cent. of alcohol, and after this it is inadvisable to drink it.

In Italy kephir or kephir-extract is placed on the market by the Borgosatollo Dairy (Brescia) and kephir dried *in vacuo* is also prepared (Rosemberger, Ger. Pat. 198,869, 1907).

KOUMIS is similar to kephir, and of equally ancient origin, but is prepared from mares' milk. In Russia there are various sanatoria which make efficacious use of large quantities of koumis. The composition of the latter has been found to be: Water, 94 per cent.; CO_2, 0·9; ethyl alcohol, 1·7; lactic acid, 0·7; lactose, 1·3 (before fermentation 5·5); fats, 1·3; proteins, 2·3 (largely peptonised); salts, 0·3.

GALAZIN is obtained by placing skim (cow's) milk, with 2 per cent. of sugar and 0·3 per cent. of beer-yeast in strong, tightly stoppered bottles, and allowing fermentation to proceed for twenty-four hours at 16°; from the second to the sixth day the proportion of alcohol rises from 0·3 to 1·5 per cent. Galazin is less nutritious than kephir or koumis.

BEER

This is another alcoholic liquor saturated with CO_2 and is obtained by fermenting aqueous decoctions of barley-malt and hops.

The ancient Egyptians were acquainted with the manufacture of beer and held it in great regard. Later it became known to the Ethiopians and the Hebrews, but the Greeks never acquired a taste for beer. The industry was taken by the Armenians from Egypt into the interior of Asia, and still later beer was manufactured in Spain and France, but it was never consumed by the Romans. In Germany beer has been made from time immemorial.

A marked improvement in the manufacture of beer dates from the time of Charles the Great, when hops were first used.

Lager beer (*see later*) was prepared as early as the thirteenth century, and its use has since greatly extended in various countries.

In England the manufacture has flourished since the fifteenth century, the famous **porter** being first made at the beginning of the eighteenth century.

The improvement made in brewing operations by the introduction of scientific methods has led to a very considerable development of the industry in Germany and elsewhere.

In all stages of the manufacture the greatest cleanliness is now practised, the walls and floors as well as the vessels being frequently disinfected by means of dilute calcium bisulphite solution (1 per cent.), or hydrofluoric acid solution, or ozone (*see* Vol. I., p. 202).

1. **A. BARLEY** [1] should satisfy the following requirements :

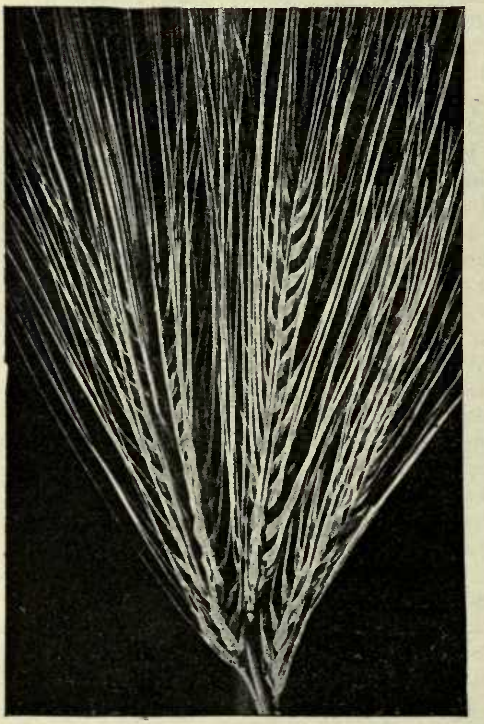

Fig. 152.

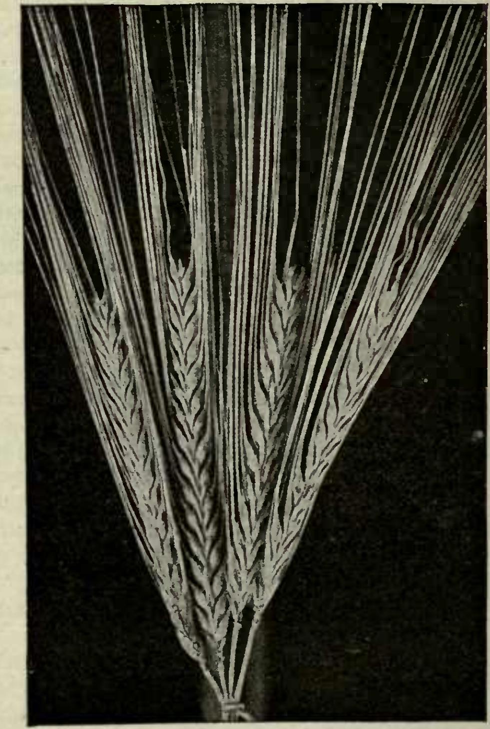

Fig. 153.

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[1] **Barley** (botanical species *Hordeum*) used for making beer is of two types : *two-rowed* (Fig. 152), in which the corns are arranged in the ear in two rows, one on each side, and *six-rowed* (Fig. 153), in which there are three rows of corns on each side of the ear. Barleys of different kinds may, to some extent, be recognised by the form of the small *basal bristle* found at the base of the corn inside the longitudinal furrow. The value of barley for brewing purposes is largely influenced by the nature of the soil, climate, methods of cultivation, and manuring. Barley is cultivated in all countries and in all climates—in Holland and also in Sicily. It is difficult to keep varieties pure, since they become modified during growth owing to crossing. Only by the rational system of selection initiated by Dr. Nilsson at the Svalöf Institute is it possible to fix different varieties with constant, well-marked characters suited to the various districts in which at one time they originated.

From a commercial point of view, the weight of a barley is of importance and good qualities give a weight of 40 grams per 1000 corns, or 62 to 67 kilos per hectolitre for thin barleys and as much as 70 kilos per hectolitre for the larger ones. The grains should have a floury and not a (*a*) When moistened and kept at 25° to 30°, 80 per cent. of the corns should germinate in forty-eight hours and 90 to 95 per cent. in seventy-two hours.

(*b*) Those are preferred which are heaviest (60 to 70 kilos per hectolitre) and contain about 62 per cent. of starch, about 10 per cent. of protein, and 12 to 14 per cent. of moisture.

The richer the barley in proteins, the less is the amount of dry extract yielded by the malt; thus a barley with 11 per cent. of albuminoids gives a malt yielding at most 76 per cent. of dry extract, whilst one with 7 per cent. of albuminoids gives a malt yielding 81 to 82 per cent. Often, however, the barleys richer in starch are poorer in nitrogen.

(*c*) The skin should be thin and the colour pale yellow, the ends of the corns not being brown.

Barley starch swells at 50°, and with water forms a paste at 80°. With diastase it begins, unlike potato starch, to saccharify as soon as it is completely transformed into paste.

B. Wheat is sometimes used, together with barley, for *pale beers.*

C. Maize is used in America after being skinned and degermed, the germ being rich in oil. Prepared maize and rice are used in Great Britain.

D. Rice is used in America and Scandinavia with the barley.

2. **HOPS.** The female flowers, dry and mature, of *Humulus lupulus* (Fig. 154) are used, these containing 10 to 17 per cent. of a powder, *lupulin* which can be separated by shaking and sieving), possessing the aromatic and bitter principles which bestow on the beer its aroma and keeping qualities.[1]

FIG. 154.

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vitreous appearance when cut through, and there should be few broken corns, as these do not germinate and become mouldy on the malting floor. Germination tests, made on 500 or 1000 corns, should show at least 95 per cent. of germinated corns in five to six days. With barley harvested under wet conditions, the ends of the corns are darkened.

The *world's production* of barley in 1906 was 31,500,000 tons, in 1910 31,000,000 tons, and in 1913 36,600,000 tons. In 1910 (and also in 1913) France produced 1,080,000 tons (17,000,000 hectolitres from an area of 737,300 hectares). In 1913 Germany produced 3,673,200 tons, Austria 1,750,000, Hungary 1,730,000, Bulgaria 300,000, Denmark 600,000, Spain 1,500,000, Great Britain 1,500,000, Roumania 600,000, Russia 12,100,000, United States 3,900,000, Canada 1,050,000, Japan 2,370,000 and Algeria 1,090,000. Italy produces on the average 220,000 tons of barley per annum and imported the following quantities of *malt* (mainly from Austria and Germany):

	1908	1910	1912	1913	1914	1916
Tons . .	12,400	17,800	19,108	15,843	18,200	8,890
£ . .	89,240	128,080	244,582	202,790	276,800	157,000

[1] In regions where hops are cultivated on an industrial scale, the agriculturists whose lands border on the hop gardens are compelled by law to destroy any male hop plants accidentally growing in their fields. The non-fertilised female flowers do not bear fruit.

The best hops are cultivated in Bohemia (at Saaz), Bavaria, Posen, Würtemberg, Baden, and Alsace-Lorraine, where they are picked towards the end of August. If they are too ripe the bracts of the hop-cones open and *lupulin* is lost. The most extensive cultivation of hops takes place in the United States.

The hop should have a bright yellowish green, and not a brown, colour, and the bracts should not be open; a too green colour indicates that the hops have been picked in an unripe condition.

3. **WATER.** Formerly water for brewing purposes was invested with a mysterious importance, but nowadays the water is tested in a much more rational and rigorous manner. Preference used to be given to moderately soft water, but now waters of medium hardness are regarded as best, as it is found that a certain quantity of calcium sulphate aids fermentation, but if the water is too hard, less extract is obtained from the

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The seeds have no value for brewing purposes, the largest hops being of least value. They should not have an unpleasant odour. Since the fresh hops contain 75 to 85 per cent. of moisture, so that they will not keep, it is necessary to dry them in the air or in ovens at 25° to 30° in a strong current of dry air, until they contain only 12 to 15 per cent. of moisture; they will then keep well, even for a year or more. Their keeping qualities may be improved by sulphuring them (with SO_2) either when dry or during the drying. Sulphuring is, however, often applied to inferior hops to mask their defects.

The better qualities are seldom sulphured and, when they are well dried, are kept tightly compressed in large sacks or in evacuated metal cylinders. They may also be kept in a very cool place (cold store).

The bitter flavour and keeping properties imparted by the lupulin of hops depend mainly on their content of *humulene*, which is a sesquiterpene, $C_{15}H_{24}$, and on that of the α- and *β-bitter acids*, which varies from 6 to 18 per cent. The α-acid is *humulene*, $C_{20}H_{32}O_5$, and the β-acid, *lupulinic acid*, $C_{25}H_{36}O_4$; both are insoluble in water and very bitter, and may be determined by Lintner's method as follows: 10 grams of an average sample of the hops are heated in a flask graduated at 505 c.c., with 350 c.c. of light petroleum (b.-pt. 30° to 50°) for six hours on a water-bath at 40° to 45°, an efficient reflux condenser being fitted to the flask. When the latter is cold, it is filled to the mark with light petroleum and shaken, the contents then being filtered. 100 c.c. of the filtrate, mixed with 80 c.c. of alcohol, is titrated with decinormal potassium hydroxide solution in presence of 10 to 15 drops of phenolphthalein solution. If much fat is present an aliquot part of the light petroleum solution is evaporated and the residue extracted with methyl alcohol, which does not dissolve the fat and, on evaporation, gives the bitter acids; these may then be weighed.

The quality and commercial value of hops are influenced largely by the nature of the soil and the quality of the manure used, as well as by the variety of the hop itself.

Chemical composition does not always give satisfactory indications for judging of the value of hops, and this is almost always done by men experienced in valuing hops. Hops give up to alcohol 22 to 30 per cent. of extract, about two-thirds of which is composed of a resin giving the bitter flavour and acting as an antiseptic towards certain bacteria injuriously affecting the keeping of the beer, although it has no influence on the yeast. The flavour of the beer is also considerably affected by the tannin contained in the hop to the extent of 2 to 4 per cent.

The determination of the ethereal extract is also employed in judging of the quality of hops; with good qualities, after evaporation of the ether, 27 to 28 per cent. of residue is left (*see above*, Lintner Test).

Germany imported 2800 tons of hops in 1908 and 2636 tons in 1909, the exports being 12,400 and 8800 tons respectively in 1908 and 1909. The United States imported 2800 tons in 1911 and exported 7000 tons.

The International Agricultural Institute of Rome gives the following statistics of hop production:

		1908	1910	1911	1912	1913	1914	1915
Germany	tons	26,340	20,411	10,628	20,563	10,618	23,237	14,563
	hectares	35,865	27,460	26,658	26,966	27,048	27,685	23,737
Austria	tons	18,748	16,512	8,613	20,146	8,564	16,444	—
	hectares	25,364	21,281	19,919	20,304	20,260	18,480	—
Hungary	tons	867	834	1,153	1,796	—	—	—
	hectares	1,142	926	1,357	2,176	—	—	—
Belgium	tons	3,869	3,102	3,075	4,612	3,355	—	—
	hectares	2,060	2,047	2,101	2,283	2,405	2,485	—
France	tons	5,157	3,232	2,630	3,973	3,568	3,191	2,227
	hectares	3,030	2,741	2,843	2,832	2,951	2,731	2,214
Great Britain	tons	23,916	15,377	16,664	18,971	12,987	25,770	12,935
	hectares	15,751	13,308	13,377	14,095	14,437	14,836	14,060
Russia	tons	4,428	2,949	3,293	4,423	7,699	6,388	—
United States	tons	19,913	22,514	23,438	24,208	28,530	19,693	26,907
	hectares	—	—	—	—	—	—	—
Whole world	tons	103,894	85,784	70,015	99,635	77,022	96,725	82,599
	hectares	84,000	68,515	67,000	69,489	69,068	71,586	66,875

The output of hops per hectare (2·47 acres) varies from 14 to 30 cwt.

Australia produces 800 to 900 tons of hops, the area under their cultivation being 500 to 600 hectares.

malt and hops. Iron is also harmful, and especially so are waters contaminated with bacteria.[1]

The principal operations in the manufacture of beer are as follow:

(1) **CLEANING OF THE BARLEY,** to remove dust, soil, stones, damaged and light corns, etc., by means of sieves, fans, etc.

(2) **STEEPING OF THE BARLEY** for two or three days in water at 11° to 12° in order that it may absorb the water necessary for germination (about 45 per cent.).

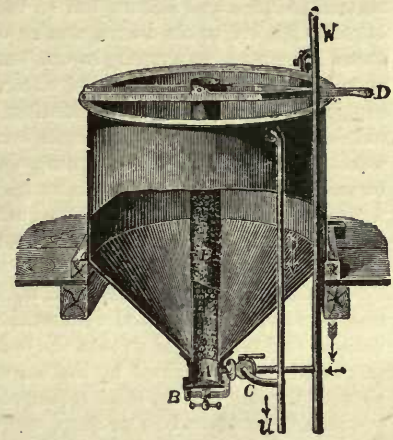

Fig. 155.

For this purpose use is generally made of the Neubecker tank (Fig. 155), made of iron plates, open at the top and cone-shaped at the bottom. In the middle is a wide perforated pipe, *E*, which is surrounded by the barley (500 to 3000 kilos). The water is supplied by the pipe *W*, and is discharged through the perforations of *E*, thus covering the barley; it is then discharged from the top of the tank through the pipe *U*, the lighter

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[1] *Water* for brewing should contain only small proportions of carbonates, since these partially neutralise the primary phosphates of the wort, whereas for the enzymic functions inherent to the mashing of the malt the acidity of the malt (primary phosphates) should be preserved. The mashing process is characterised by the degradation of the starch by diastase and by the decomposition of the protein substances by means of peptases. The secondary phosphates are alkaline to methyl orange (the primary phosphates being neutral) and hinder these enzymic processes.

Carbonates tend to diminish the acidity, thus: $4KH_2PO_4 + 3CaCO_3 = 3CO_2 + 3H_2O + Ca_3(PO_4)_2 + 2K_2HPO_4$. Sulphates, however, tend to restore the acidity and transform the secondary into primary phosphates: $4K_2HPO_4 + 3CaSO_4 = Ca_2(PO_4)_2 + 3K_2SO_4 + 2KH_2PO_4$; the beneficial effect of gypsum is thus explained.

The carbonates (calcium bicarbonate) may be eliminated by boiling the water or by passing air for half an hour through the water at 85°, all the calcium carbonate and most of the magnesium carbonate being thus deposited; if the temperature is lowered to 60° magnesium carbonate redissolves, so that the water should be filtered hot. The cautious decomposition of the carbonates with mineral acids or, better, with lactic acid has been suggested.

The proportion of gypsum present in the water is often increased artificially. For pale beers (Pilsener) the water is preferably less hard, even though it contains only little gypsum. Excess of the latter affects the flavour of the beer, as it is left finally as potassium sulphate (*see above*), which has a decided taste; this is readily observed on adding 20 to 25 grams of potassium sulphate per hectolitre to beer made with a moderately soft water.

In the case of dark beers the influence of the salts of the water is less apparent, since the torrefied malt is more acid and the caramel and sugar impart to the beer a marked taste, which masks other flavours. Even for dark beers, however, a water of only moderate hardness is to be preferred.

The water of the Munich breweries contains a medium proportion of carbonates (the residue, 28 grams per hectolitre, contains 25 grams of carbonates) and very little gypsum; artificial increase of the latter is, however, never suggested, although common in Britain.

Also for steeping barley a moderately hard water is best.

The compositions of various waters are as follows (parts per 1,000,000):

	Good	Medium	Bad
Dry residue	250–450	450–550	550–700
Ferric oxide and alumina (Fe_2O_3,Al_2O_3)	0–1·5	1·5–2·5	3
Lime (CaO)	120–150	150–200	200–300
Magnesia (MgO)	20–50	50–80	80–120
Sulphuric acid (SO_3)	20–60	60–80	100–200
Ammonia	—	—	trace–1·5
Nitrites and Nitrates	—	0–0·5	0·5–1·5
Organic matter (as oxygen absorbed)	0·4–1·5	1·5–2·0	2–3
Hardness (French degrees)	15–25	25–35	35–50
Number of bacteria per 1 c.c.	50–500	500–4000	4000–10,000

These numbers are only indicative and must not be taken too strictly.

floating corns being carried away. After seven or eight hours the water is run off through the tap *C*, and the moist barley left exposed to the air for five or six hours. Fresh water is then introduced and left for ten to twelve hours, after which it is run off and the grain exposed for five or six hours, and so on. This procedure is continued for thirty to fifty hours in summer or seventy to one hundred hours in winter, the corns having in that time absorbed about 40 per cent. of water. Steeping of the barley in lime-water has been suggested as a means of preventing abnormal fermentations (Windisch, 1901) and of obtaining beer of improved aroma and flavour. In some cases steeping is preceded by washing of the barley in running water in rotating cylinders, or else compressed air is forced into the steeping vessels at frequent intervals, so as to stir the barley. The steep-water becomes yellowish brown and acid, and after some time undergoes lactic and butyric fermentations. At the end of the operation, the barley is discharged through the lower aperture, *A*, by undoing the screw, *B*, and raising the tube *E*, by means of the lever, *D*.

(3) **GERMINATION OF THE BARLEY.** The steeped barley is carried to the spacious *malting floor*, which is fitted with numerous windows to allow of the renewal of the air when desired, and is arranged so that the temperature may be maintained constant at 12° to 16°; this end is often attained by the use of semi-underground cellars, which should, however, be well ventilated. On the impermeable floor (of cement or asphalte), the barley is spread out in a layer 50 to 60 cm. deep, and on the second day the mass is moved with wooden shovels so as to reduce the depth to 30 to 35 cm., this being further reduced to 15 cm. on the third day. Every eight or ten hours the grain is turned, the floor being kept well ventilated. The temperature gradually rises, but should not be allowed to exceed 20°; if necessary it may be moderated by turning more often and thinning out the barley. After the second day the radicles begin to sprout and later the plumule. In eight to ten days the rootlets become twice or three times as long as the corn and the transformation of nitrogenous material into diastase is at its maximum (Fig. 156 shows the various stages in the germination of barley). The germination should then be interrupted so as not to lose any part of the diastase formed, the *green malt* then containing about 40 per cent. of moisture. A floor of 20 sq. metres is sufficient for only 1000 litres of steeped grain. If the *piece* dries too much, it is moistened by sprinkling with water. In order to prevent mould-growth when the floor is free, it, and also the walls, are washed with 1 per cent. calcium bisulphite solution, the floors being then well dried by ventilation.[1]

FIG. 156.

The germination is now sometimes carried out on the *pneumatic system*, use being made of the Galland apparatus (Figs. 157 and 158), which consists of a double sheet-iron drum, *T*, rotated by means of the wheels, *b* (two rotations, each occupying forty minutes, every six to eight hours). The inner drum is perforated and is filled to the extent of four-fifths with barley from the steeping tank, *W*; along the axis of the cylinder passes a pipe which is also perforated. Air sucked in by a fan, *Z*, is moistened in *A* by means of pulverised water, and from *L* passes into the jacket of the drum, then through the perforations and the

[1] In Germany beer must be made from malted barley alone; in 1912 the German breweries used 1,300,000 tons of barley (almost exclusively two-rowed), of which a small part only was imported from Austria.

Barley contains 60 to 70 per cent. of starch, 0·5 to 2 per cent. of saccharose, 2 to 3 per cent. of fat, and 8 to 14 per cent. of proteins.

At least 95 per cent. of the barley corns should germinate (*germinative capacity*), the *germinative power*, *i. e.*, the rapidity of germination, also being of importance; with a good barley, not less than 95 per cent. of the corns should germinate within three days. A barley with a germinative capacity of 85 to 90 per cent., and a similar germinative power is preferable to one having a germinative capacity of 100 per cent. and a germinative power of only 70 per cent.

In general barley rich in proteins is poor in starch and hence yields a malt of low extract, whereas protein-poor barley is rich in starch and gives a malt yielding a high extract. During mashing the starch passes almost completely into solution, whilst only about one-third of the protein substances is dissolved, the remaining two-thirds being found in the grains.

Barley contains a diastase capable of saccharifying dissolved starch, but incapable of dissolving starch; the latter end is attained by means of the diastase formed during the germination of the barley.

grain to the central pipe, *m*. Thence it proceeds to *S*, and so through the fan *Z* to the shaft; a thermometer here shows the temperature of the air, and if this becomes too high the speed of the fan is increased. If 100 kilos of barley is taken and the air enters at 12° and issues at 20°, 4500 cu. metres of air is required per hour; if the air is to leave at 16°, 10,000 cu. metres per hour is necessary. The germination lasts eight to nine days.

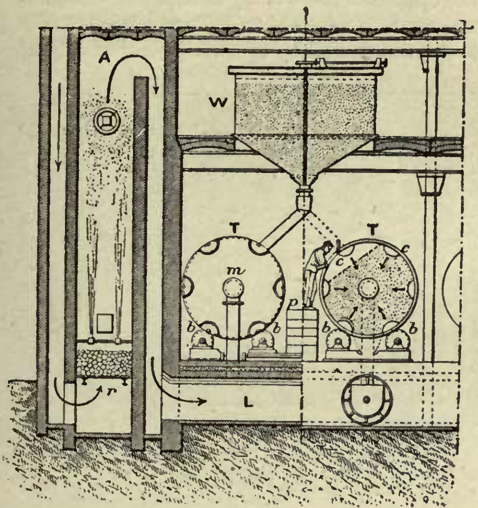

Fig. 157.

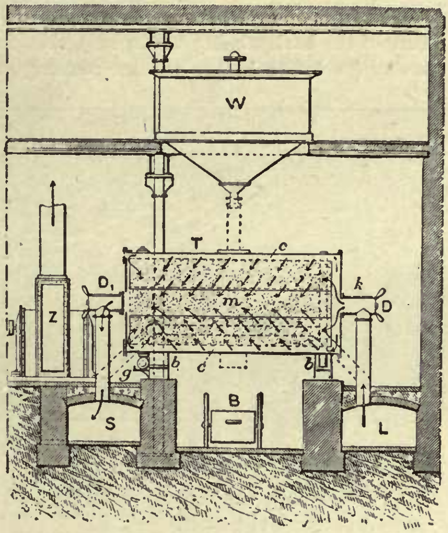

Fig. 158.

To stop the germination, a current of dry air, heated to 22° to 25° or mixed with gas rich in CO_2 (to diminish the supply of oxygen), is supplied; in a short time the moisture content of the grain is reduced from 40 per cent. to 20 to 25 per cent.

For a malting to give continuously 2000 to 5000 kilos per day, three to four steeping-tanks are used, these feeding six to eight Galland drums arranged in batteries (Fig. 159); 6 to 10 horse-power is required for turning the drums, driving the fans, etc.

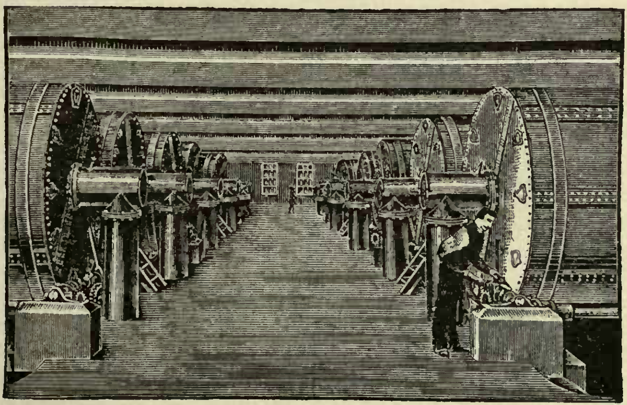

Fig. 159.

The water necessary for steeping amounts to about 10 to 12 times the weight of the barley, rather less being required to moisten the air for pneumatic malting. The steep-water may hence be used again for the latter purpose if at any time the water-supply is scarce.

Another system of malting, used especially in France, is that of Saladin (shown in perspective in Fig. 160, while Fig. 161 shows a longitudinal section of one of the vessels, and Fig. 162 a transverse section of the vessels). There is one vessel, made of concrete and fitted with a perforated false bottom of sheet-iron, for each day that the germination lasts (eight to nine days). These vessels, *B*, communicate under the false bottom with a channel containing a fan which draws moistened air through the mass of barley in the vessel (50 cm. deep). Above each vessel is a slow mechanical turner, *A*, with a number of screws which rotate in the barley as the turner passes along the vessel. The turner may be transported from one vessel to another and is put into operation twice a day at first (the temperature of the barley being 12° to 14°), then four times a day (at 15° to 18°), and finally twice a day (at 18° to 15°). In some maltings a saving is effected by operating the fan only at intervals—when the temperature rises. Dry air, drawn along the channels, *S*, is finally passed through the malt.

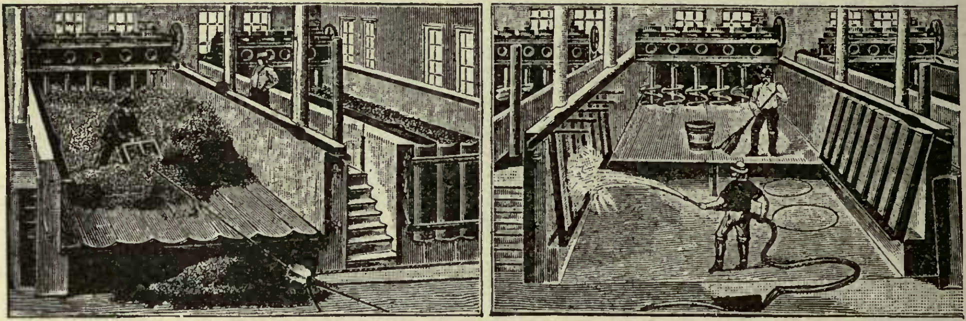

FIG. 160.

The advantages of the various mechanical processes over the old system of malting are that they may be worked continuously and at any season of the year, while they occupy less space, allow of efficient regulation of temperature, economise labour and general expenses and diminish the percentage of waste.

(4) **KILNING OF MALT.** The germinated barley is too moist to keep sound, and as breweries require large stocks of malt this must be dry and capable of being kept. If the moisture is reduced to 6 per cent. by air alone the germination process is stopped, and on subsequently raising the temperature to 60° a slight diastatic saccharification occurs, this being greater in amount if the moisture is kept at 12 to 15 per cent.; beyond 70° the diastase is destroyed and certain substances formed which give good flavour, aroma and fullness of taste to the beer and at the same time furnish food for the yeast. When the temperature exceeds 100° part of the maltose is caramelised—for the making of *dark beers*—and a considerable amount of nitrogenous substances, which would cause the beer to keep badly, rendered insoluble.

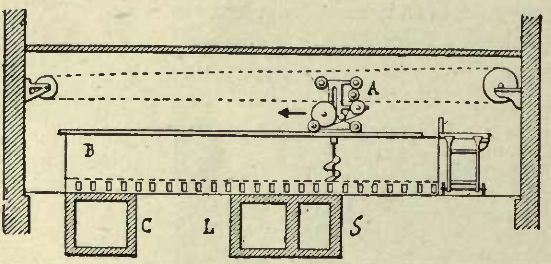

FIG. 161.

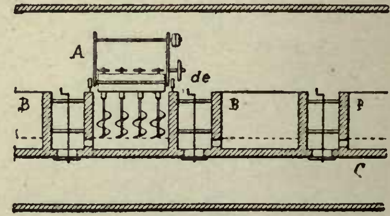

FIG. 162.

In order not to destroy too much of the diastase and to make malt suitable for *pale beers* the drying must first be conducted with only slightly warm air. When the proportion of moisture has reached 5 to 6 per cent. the diastase is able to withstand a temperature of 60° to 70° without losing much of its activity, whilst if the malt is heated when it contains too much moisture (15 to 20 per cent.) the diastase is rapidly destroyed. The drying is carried out in a current of warm air (or of air mixed with the hot gases from a coke or anthracite fire), which passes through the green malt placed in layers 15 to 20 cm. deep on wire or tile floors, often arranged one above the other. Above the upper floor is a chimney, which increases and facilitates the draught started by suitable fans. The air is heated by passing directly over a fire or through batteries of tubes heated in the usual way. During the drying the malt is turned by a suitable mechanical device, at first every two hours and later on continuously. The temperature of the air gradually rises, during the course of eighty-four to ninety hours, by 30° to 35° (during the first few hours germination still proceeds feebly, causing increase in the diastase), and ends at 100° to 110° (for dark beers). Drying is usually effected in less than forty-eight hours, and it is only beyond 80° that the diastase partially loses its saccharifying properties (at 90° it loses 50 per cent. and at 100° 85 per cent.); this loss is, however, an advantage, since a too highly diastatic malt leads to excessive saccharification and hence to increased attenuation in the subsequent fermentation, so that the beer tastes less full. The peptases also are destroyed beyond 90°, so that the nitrogenous substances are dissolved to a less extent and the beer hence keeps better.

Fig. 163 shows diagrammatically a section of a two-floor malt-kiln in which the air is heated in the tubing, *t*, surrounding the ducts carrying the hot fumes from the coal burning on the grate, *F*. The hot air then traverses the malt on the floors, *B* and *C*, and issues from the chimney, *D*, the turning apparatus, *a*, being kept in motion meanwhile. To obtain 100 kilos of dry malt in twenty-four hours (maximum temperature 90° to 100°) 20 kilos of coal are required. For making *dark beers* of the Munich type part of the kilned malt is further roasted at about 200° in suitable rotating iron cylinders heated by direct fire; this treatment leads to the formation of caramel, which colours the beer, the malt being then called coloured malt. The temperatures on the malting-floors and kiln are registered by automatic devices which construct diagrams showing the temperature at any particular moment.

Nowadays malt for *pale beers* is sometimes heated only to 25° to 30°.

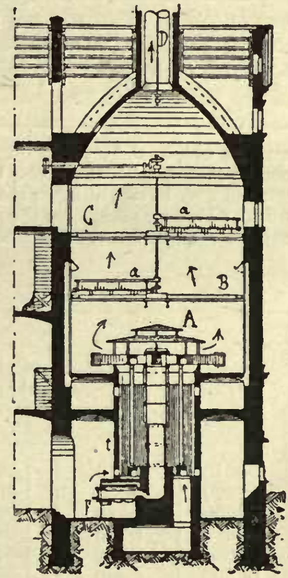

Fig. 163.

The kilned malt leaves the kiln with 2 to 5 per cent. of moisture, and is then cooled and stored in silos or large bins. A malt kept for only one or two months is to be preferred to an older one.[1]

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[1] The *commercial value of a malt* is determined largely by its yield of *extract*, which is measured as follows: 45 grams of ground malt are placed in a tared flask with 200 c.c. of water, the temperature being kept at exactly 45° for half an hour and then raised 1° per minute up to 70°, this temperature being maintained until the liquid no longer gives a blue colour with iodine; the time required at 70° to reach this point is noted (*saccharification test*). The mass is then cooled and water added to bring its total weight up to 450 grams; after mixing and filtering through a dry filter, the density of the liquid is determined at 15° and by Windisch's or Schulze's tables the corresponding quantity of extract deduced. The latter may also be obtained from Balling's tables (*see below*), note being taken that they yield low values, the deficit being 0·08 gram per cent. for specific gravities up to 1·01; 0·345 for specific gravities up to 1·05; 0·48 for specific gravities up to 1·06; and 0·4 for specific gravities up to 1·08. If the maltose is to be determined directly, 10 grams of the filtered saccharine liquid (corresponding with 1 gram malt) are diluted to 100 c.c., various quantities of this liquid being then titrated with Fehling's solution, 1 c.c. of which corresponds with 0·0075 gram of maltose.

C. Lintner (1886–1908) has modified the Kjeldahl method for determining the *diastatic power of malt* as follows: 25 grams of the ground malt are extracted for 6 hours with 500 c.c. of water at the ordinary temperature, the mixture then being filtered; 2 c.c. (for pale malts) or 8 c.c. (for dark malts) of the filtrate is added to 100 c.c. of 2 per cent. soluble starch solution and the mixture left for exactly half an hour, at the end of which time 10 c.c. of $\frac{N}{10}$ caustic soda solution is added. Into a number of test-tubes, each containing 5 c.c. of Fehling's solution, are introduced varying quantities of the saccharified starch solution (*e. g.*, from 1 to 6 c.c.); the tubes are next immersed for ten minutes in a boiling water-bath and then taken out, and the precipitated cuprous oxide allowed to settle; it can then be seen in which of the tubes the Fehling's solution is just completely reduced and in which it is just not reduced. A more exact result

Malt kilned with fumes direct from a coal fire communicates to the beer a certain flavour from the smoke. Also, when coal is employed which contains arsenic, the latter becomes deposited on the malt and hence finds its way into the beer. Arsenic may also be present in the glucose often used in brewing; in this case it is introduced by the employment of arsenical sulphuric acid in the manufacture of the glucose from starch.

(5) **CLEANING AND GRINDING.** Before the malt is mashed it is freed from dust and rootlets by means of rotating drums of metal gauze (a kind of sieve) furnished with fans. It is then ground, but not too finely, the husks being kept whole as far as possible, since they serve in the subsequent operations as filtering material; if the malt is ground too fine it cannot be exhausted, as the liquid will not drain off. A suitable form of mill is the Excelsior Mill, made by Messrs. Krupp (Figs. 164 and 165). The shaft, *g*, fitted with fast and loose pulleys, *s* and *t*, may be shifted from right to left or *vice versa* through the stuffing-boxes, *m*, by means of the lever, *d*. One toothed disc, *a*, is fixed, whilst the other, *b*, rotates with the axis, *g*, and is so adjusted that the teeth pass through the tooth spaces of the other disc. The malt from the hopper, *f*, falls between the two discs, where it is

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may be obtained by using quantities of the saccharified starch solution intermediate to those corresponding with these two tubes. When 0·1 c.c. of the cold water malt extract, acting for one hour on 10 c.c. of 2 per cent. soluble starch solution, forms just sufficient maltose to reduce 5 c.c. of Fehling's solution, the malt is said to have the diastatic power 100; if 0·2 c.c. of the malt extract is required, the diastatic power is taken as 50, and so on.

BALLING'S TABLE

Sp. gr. at 17·5°	Degrees Balling or grams of saccharose per 100 grams liquid	Sp. gr. at 17·5°	Degrees Balling or grams of saccharose per 100 grams liquid	Sp. gr. at 17·5°	Degrees Balling or grams of saccharose per 100 grams liquid	Sp. gr. at 17·5°	Degrees Balling or grams of saccharose per 100 grams liquid
1·0010	0·250	1·0210	5·250	1·0410	10·142	1·0610	14·904
1·0020	0·500	1·0220	5·500	1·0420	10·381	1·0620	15·139
1·0030	0·750	1·0230	5·575	1·0430	10·619	1·0630	15·371
1·0040	1·000	1·0240	6·000	1·0440	10·857	1·0640	15·604
1·0050	1·250	1·0250	6·244	1·0450	11·095	1·0650	15·837
1·0060	1·500	1·0260	6·488	1·0460	11·333	1·0660	16·070
1·0070	1·750	1·0270	6·731	1·0470	11·571	1·0670	16·302
1·0080	2·000	1·0280	6·975	1·0480	11·809	1·0680	16·534
1·0090	2·250	1·0290	7·219	1·0490	12·047	1·0690	16·767
1·0100	2·500	1·0300	7·463	1·0500	12·285	1·0700	17·000
1·0110	2·750	1·0310	7·706	1·0510	12·523	1·0710	17·227
1·0120	3·000	1·0320	7·950	1·0520	12·761	1·0720	17·454
1·0130	3·250	1·0330	8·195	1·0530	13·000	1·0730	17·681
1·0140	3·500	1·0340	8·438	1·0540	13·238	1·0740	17·909
1·0150	3·750	1·0350	8·681	1·0550	13·476	1·0750	18·136
1·0160	4·000	1·0360	8·925	1·0560	13·714	1·0760	18·363
1·0170	4·250	1·0370	9·170	1·0570	13·952	1·0770	18·590
1·0180	4·500	1·0380	9·413	1·0580	14·190	1·0780	18·818
1·0190	4·750	1·0390	9·657	1·0590	14·428	1·0790	19·045
1·0200	5·000	1·0400	9·901	1·0600	14·666	1·0800	19·272

Correction of Degrees Balling for Various Temperatures

Determination made at temperature of Deg.	Correction of degrees Balling	Determination made at temperature of Deg.	Correction of degrees Balling	Determination made at temperature of Deg.	Correction of degrees Balling	Determination made at temperature of Deg.	Correction of degrees Balling
4	− 0·43	11	− 0·22	17·5	—	24	+ 0·27
5	− 0·40	12	− 0·19	18	+ 0·02	25	+ 0·32
6	− 0·37	13	− 0·16	19	+ 0·05	26	+ 0·37
7	− 0·34	14	− 0·13	20	+ 0·09	27	+ 0·42
8	− 0·31	15	− 0·10	21	+ 0·13	28	+ 0·48
9	− 0·28	16	− 0·06	22	+ 0·17	29	+ 0·54
10	− 0·25	17	− 0·02	23	+ 0·22	30	+ 0·60

ground, the ground malt (*grist*) being discharged at *n*. For the sake of economy the discs are toothed on both faces, so that when one face is worn the other may be used.

The total loss in weight suffered by the barley during steeping, germination, kilning, cleaning, and grinding amounts to about 20 per cent.

(6) **MASHING.** This consists in subjecting the ground malt to the action of warm water so that the diastase may act on the starch and convert it into soluble products. The temperature at which the maximum extract is obtained is about 65°, whilst at 55° the starch is only very slightly attacked by diastase, and above 70° diastase loses its saccharifying properties very largely and the wort filters through the grains (husks; *see later*) with difficulty—this effect is aggravated by coagulation of part of the proteins. The quantity and quality of the water have an influence on the mashing, the presence of calcium sulphate facilitating the formation of maltose and maltodextrins and increasing the amount of nitrogenous substances dissolved. From 1 ton of malt 20 to 30 hectolitres of beer are made.

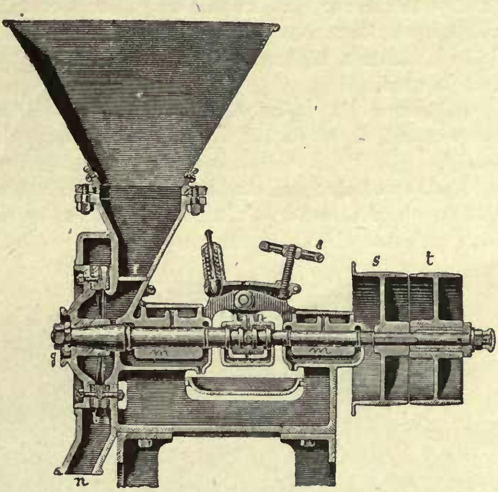

FIG. 164.

There are two systems of mashing: the **infusion** method (at 65° to 72°), used only in top-fermentation breweries, and the **decoction** system, used for bottom-fermentation and sometimes for top-fermentation beers, and with highly diastatic malt or when unmalted barley is used with the malt.

(I) The **infusion process**, used largely in England and Scotland, less in France and still less in Germany, is usually carried out in one of two ways: (i) *Rising infusion*, where the malt is first mixed to a paste with 10 per cent. of cold water and then with hot water in the ratio of two parts of water to one part of malt, so that a temperature of 40° is attained. To raise the temperature of 1 kilo of malt (which has a specific heat of about 0·5) from 20° to 40° requires 10 Calories, which can be supplied by 2 litres of water at 45°, the latter falling to 40° on losing 10 Calories; owing, however, to unavoidable loss of heat, water at 48° to 50° should be used.

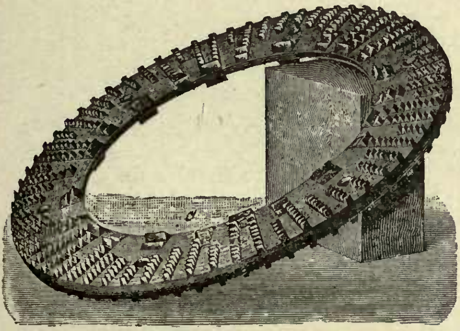
FIG. 165.

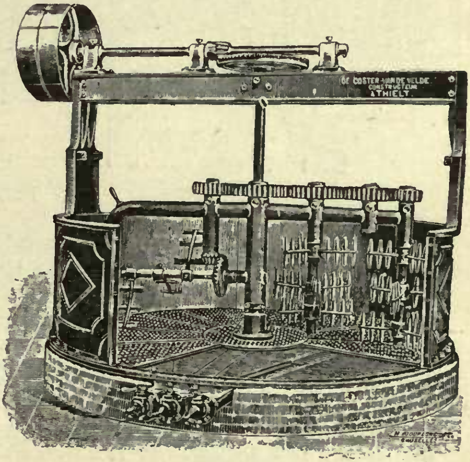

FIG. 166.

This mixing is done in a circular mash-tun of metal or wood, furnished with a perforated false bottom several centimetres above the true bottom, in which are fitted the pipes supplying the hot water (Fig. 166). The mashing and subsequent mixing are effected by efficient mechanical stirrers or rakes.

As soon as the mash has reached the temperature of 40° water at 80° is gradually introduced, the temperature being raised to 63° to 65° in half an hour. It is next mixed for sixty to seventy minutes, the liquid being then discharged by opening the taps under the false bottom so that the liquid passes through the grains and is conducted to the copper. The residue in the tun is mixed for fifteen minutes with water at 75°, the liquid being run off and the grains finally washed with water at 85°, all these extracts passing to the copper. In this way almost complete saccharification is attained and the subsequent fermentation produces considerable attenuation. If a less attenuation is desired, either a higher temperature (72° to 73°) is used in place of 65°, or high-dried malt is used.

(ii) *Descending infusion*, which is rarely used, consists in bringing the mass directly to a temperature of 65° to 70° with very hot water and then allowing it to fall slowly to 35° to 40°.

Neither of these methods admits of the use of rice or maize, the starch of which is attacked by diastase only after the starch has been heated with water to 80° to 85°. Hence with such material the decoction process is used.

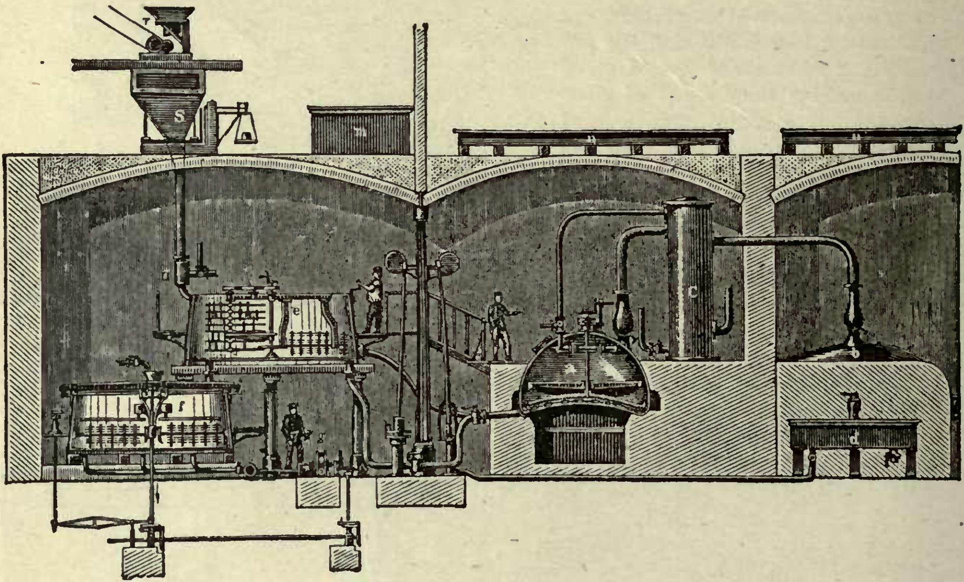

Fig. 167.

(II) **Decoction Process.** This is largely used in North Germany, Austria, and Belgium, and allows of the use of unmalted barley, rice, maize, wheat, etc.

The malt grist is first mixed to a paste with cold water so as to dissolve the diastase, this being carried out in a metal vessel without a false bottom; by the addition of small quantities of boiling water the temperature of the mass is raised gradually to 35°. From one-third to one-half of the turbid wort (*Dickmaische*) is transferred to a double-bottomed copper heated with steam. In many cases coppers with direct-fire heat are used, these being furnished with chains which scrape on the bottom and so prevent caramelisation of the mass which settles (Fig. 167 shows a complete decoction or infusion plant). The wort transferred to the copper is boiled for twenty to forty minutes and is then returned to the original tun, where it raises the temperature to about 55°. Another one-third or one-half is similarly removed, boiled, and returned, the temperature being thus raised to 65°; the saccharification has then reached a maximum and the mash become thinner. The complete disappearance of starch is controlled by the reaction with iodine. About one-half of the wort is again removed, boiled, and returned, the temperature being thus raised to 75°. During all these operations continual stirring is maintained. The greater the number of decoctions made the greater will be the density of the wort and the darker the beer. The turbid wort is either allowed to deposit in tuns with false bottoms, as shown in Fig.

166, or passed through filter-presses (*see* Sugar Industry) to clarify it, the *grains* remaining in the form of cakes being well washed.[1]

When considerable quantities of other cereals are to be used with the malt use is made of a Henze pressure apparatus, as described under Distilling (Fig. 106, p. 142).

The wort thus obtained is boiled with a certain quantity of hops until a certain degree of concentration has been effected. This boiling finally destroys the diastase, intensifies the colour of the wort and aerates it, and oxidises various substances producing acid bodies; it completely sterilises the liquid, which is also clarified owing to the precipitation of nitrogenous substances, partly by the tannin of the hops.

The *decoction of the hops* is carried out in a separate vessel, the boiling liquid being continually circulated until the hops are exhausted. The decoction is then added to the boiling wort, principally towards the end of the operation; if added earlier the hop extract loses some of its aroma. Direct addition of the hops to the copper is still practised, although the method is not a very rational one; it is better to pass the boiling wort from time to time into a separate vessel containing the hops and then back to the copper, this procedure being repeated until the hops are exhausted.

In general, 400 to 500 grams of hops are used per hectolitre of beer, or 1·2 to 2·5 kilos for every cwt. of malt mashed. More hops are usually employed for beers to be kept for some time (*lager beer, stock ale*) than for *draught beer,* and more for beers of the Pilsen type than for those of the Munich type. The *lupulin* powder contained in the hop gives up resins and essential oils, while the leaves give tannin and the stalks somewhat bitter substances; the whole gives the bitter taste and aroma of the beer, and causes the latter to keep better. A temperature of 75° (Pasteur) is sufficient to sterilise a hopped beer, since the resins have a marked antiseptic action.

The *boiling of the wort* is carried out in copper vessels (*see* Fig. 167, *a*) heated by direct fire or by indirect steam (passed through coils or through the double bottom of the copper), the boiling being continued for four to six hours with dilute worts (infusion), and only one and a half to two hours with the more concentrated decoction worts; as a rule boiling is continued until the density reaches a certain value for the particular kind of beer to be made (*see later*). The temperature during boiling should be gradually raised and registered. In many modern breweries there are automatic registering thermometers which show the whole course of these operations. When the boiling is finished the wort is allowed to stand for a time, and the Inland Revenue officials then generally make their first measurements (they calculate that 1 kilo of dry malt should give 25 litres of wort with a density of 1° Balling, 5 litres at 5°, etc., an allowance being made of 10 per cent.). The copper is then discharged, the hops being strained off, and the wort pumped to the *cooler,* which is usually at the top of the building. These coolers are large shallow vessels of iron (or copper or wood) in which the coagulated proteins are deposited; the temperature here is not allowed to fall below 55° to 60°, otherwise contamination with harmful organisms (butyric, lactic, etc.) might occur. In Italy the tax on the manufacture of beer is calculated from the volume, temperature, and specific gravity of the wort in the cooler (*see later*). In the cooler, part of the water evaporates, this being as much as 4 per cent. in the summer. The wort is next cooled rapidly by suitable refrigerators to 2° to 3° (for bottom fermentation) or 12° to 15° (for top fermentation). One form of refrigerator which is much used consists of a number of superposed, communicating horizontal tubes (Fig. 168). In the tubes of the upper half water circulates, and in those of the second half brine at a temperature of — 6° or — 8° from a refrigerating machine (*see* Vol. I., p. 260). The wort flows down in a thin skin over the outside of the tubes, meanwhile dissolving an appreciable quantity of air. The cooled and aerated wort flows down to the fermenting vessels placed in cool rooms; for bottom fermentation these are cooled to about 0° by pipes conveying cold

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[1] The *grains* are composed of the whole of the husks of the malt, coagulated proteins, pentosans, fat, maltose, and dextrin. They serve as excellent cattle-food, but if not consumed in the course of 24 hours, they undergo change; they may, however, be placed in silos or dried in a suitable apparatus (*see* Fig. 151, p. 183). *Wet grains* contain 70 to 80 per cent. of water, 4 to 6 per cent. of protein, 1 to 3 per cent. of fat, 8 to 14 per cent. of extractive substances, 1 to 3 per cent. of ash, and 3 to 9 per cent. of cellulose. *Dried grains* contain 6 to 18 per cent. of water, 17 to 26 per cent. of protein, 4 to 9 per cent. of fat, 35 to 55 per cent. of extractive substances, 3 to 12 per cent. of ash, and 9 to 20 per cent. of cellulose; they have a brown colour, a pleasing odour of new bread, and a sweet taste; they make a good fodder to follow wheat or oat bran.

brine. The wort from the coolers is turbid and should be filtered through conical cloth bags or filter-presses. In some modern breweries the coolers are omitted in order to avoid any possible contamination (which is, however, difficult with hopped wort at 60°) and the wort is passed direct from the copper to the closed refrigerator and the filter-press, aeration being afterwards effected with air filtered through cotton-wool.

The refrigerators consume considerable quantities of water, and where this is scarce the warm water from the refrigerators is cooled by means of pulverisers or by causing it to flow down over twigs, the evaporation thus caused often lowering the temperature below that of the air (*see* section on Sugar). The boiling of the wort has hence effected a concentration, the preparation of a sterile (aseptic) liquid, and the extraction of the useful principle of the hop, the tannin of which has partially precipitated the proteins. If pale beer is to be brewed the wort may, if necessary, be clarified during the boiling by the addition of a little tannin. During the cooling on the coolers the wort takes up the oxygen necessary for the oxidation of the resins, for clarifying it and, more especially, for aiding the development and multiplication of the yeast during the initial stages of the fermentation.

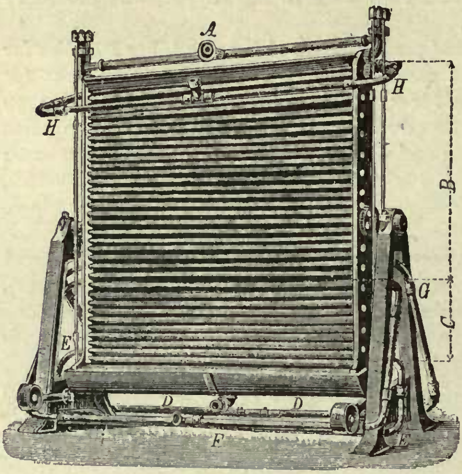

Fig. 168.

Contact of the wort with tin, *e. g.*, tinned vessels, is to be avoided, as turbidity of the beer may be caused thereby, especially if the wort is acid or rich in carbon dioxide.

FERMENTATION. From the density (degrees Balling) or the dry extract of the wort, the *extract* yielded by the materials may be deduced, and, under favourable conditions, the dry extract amounts to about 70 per cent. of the weight of the malt, whilst with bad working it may be as low as 45 per cent. When ready for fermentation the wort contains mainly maltose, maltodextrins, dextrins, a little saccharose, glucose, and levulose, besides nitrogenous substances partially peptonised and transformed into amino-acids; also lactic acid and potassium phosphates. Fermentation with yeast converts the carbohydrates more or less completely into alcohol and carbon dioxide.[1]

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[1] In addition to what has been said on pp. 133 and 146 on ferments and yeasts in general, the following is of interest, especially to the brewing industry:

All yeasts which attack only saccharose, maltose, glucose, and levulose, giving alcohol and carbon dioxide, are *feebly attenuating* yeasts of the so-called Saaz type (*e. g.*, the beer-yeasts of Liége, which yield fairly full-tasting sweet beers containing little alcohol). Other yeasts are also capable of fermenting the combined maltose of maltodextrins by means of a special enzyme studied by Delbrück, *maltodextrinase;* these yeasts give the maximum attentuation and form the so-called Frohberg type, producing alcoholic, highly attentuated beers even from weak worts. Between these types—Saaz and Frohberg—there exist intermediate ones giving in 4 days at 25° to 27°, well-defined attentuations in a *normal wort.*

Certain other yeasts are capable of fermenting dextrin combined as maltodextrins, since they contain an enzyme which Delbrück has termed *dextrinase.* Such is the *Schizosaccharomyces Pombé*, separated from the millet beer of the Egyptians. These yeasts constitute the so-called Logos type. *Wild yeasts* are all strongly attenuating and may produce turbidity in finished, slightly fermented beers, which they referment. The yeasts intermediate to the Saaz and Frohberg types, and also Frohberg yeasts themselves, are especially active in the secondary fermentation; they increase the apparent fullness of the beer, even when this is light, and maintain a continuous and desirable evolution of carbon dioxide by slowly fermenting the maltodextrins and even dextrins. In order to grow and multiply, yeasts require, in addition to carbohydrates and free oxygen, nitrogenous substances, but they cannot make use of nitrates, or ammonium salts, or even the true proteins; they can, however, utilise the decomposition products of the latter, namely, the *amino-acids* (such as asparagine) produced by the proteolytic enzymes secreted by healthy yeasts. They require also mineral substances, *e. g.*, calcium and potassium phosphates.

The oxygen of the air is, as has been said, indispensable to the development and multiplication

The concentration of the wort most favourable to the multiplication of yeast is 15° Balling (corresponding with a specific gravity of 1·06).[1] A too dilute wort or one prepared with an excessive proportion of non-germinated grain has not sufficient assimilable nitrogenous food (amino-acids), and this is remedied by the addition of *zymogen*, which is a commercial product. During the period when the yeast develops (first stage of the fermentation) little alcohol and much carbon dioxide are produced.

Two distinct methods of fermentation are in use: *top fermentation*, used generally in Great Britain, Belgium, and Holland, and largely in France, and also, at one time, exclusively in Italy; and *bottom fermentation*, usually employed in Germany, Austria, and Denmark, and in general use in countries where beers of the Munich and Pilsen types are made. In hot countries it is easier to regulate bottom fermentation (by refrigeration) than top fermentation, since in summer the temperature of the air is often high enough to have an injurious effect on top fermentation. Hence, as a refrigerating plant is necessary, the bottom fermentation system is preferable.

The difference between *bottom* and *top yeasts* is that the latter are covered with viscous, mucilaginous substances and readily stick together and carry bubbles of carbon dioxide developed in the wort to the surface and so produce a rapid fermentation; the former, however, fall to the bottom of the fermenting vessel, and even under the microscope are not found in large masses. Top yeasts develop well only at temperatures above 12°—best at about 24°—and effect complete fermentation in four to six days, whilst the bottom yeasts develop below 10° and, after the vigorous primary fermentation at 6° to 8° (eight to ten days for Munich beer, ten to fourteen for Vienna beer, and twelve to sixteen for Pilsen beer), continue the maturation of the beer for two or three months by a secondary fermentation at a low temperature (0° to 2°); this procedure gives beers of less attenuation which can be produced or consumed even in summer (*lager beer*). Top-fermentation beers are almost always more highly attenuated, are consumed at once (*draught beer*), and are made more especially in the cold weather; they can, however, be kept, and in some cases stock beers are made on this system.

The advantages and disadvantages of the two processes are as follow:

Top fermentation does not require costly refrigerating plant, and hence lends itself to the construction of small breweries; further, the beer can be sold immediately, and the capital, although small, thus frequently renewed each year. The control and successful working of top fermentation are, however, more difficult, owing to ready contamination with numerous harmful bacteria which find at 15° to 20° the most favourable conditions for their development, especially in the summer; in bottom-fermentation beers only yeasts can develop at 0° to 2°.

With top fermentation, in which at first yeasts of the Saaz type and those intermediate to the Saaz and Frohberg types predominate, there develop later bacteria and also Frohberg yeasts (especially during the secondary fermentation), and both of these render difficult the preparation of a clear beer which does not become turbid after fermentation; on the other hand, a bright beer is easily and naturally obtained by bottom fermentation. In summer then, unless an abundant supply of cold water and also cool cellars are available, and rigorous precautions and disinfection are resorted to, it is very difficult to prepare top fermentation beer, whilst the low temperature required for bottom fermentation can be attained at any season of the year by refrigerating plant. Bottom fermentation gives

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of yeast, and well-aerated worts facilitate the multiplication during the first few days, when only CO_2 and H_2O are produced; when, however, the supply of free oxygen diminishes or ceases, the yeast produces more especially alcohol and carbon dioxide. There are also saccharomyces which are solely aerobic and form membranes on the surface of the wort, producing only carbon dioxide and water and destroying the alcohol produced by other yeasts.

[1] The strengths of the worts for beers of different types are: 9° to 10° Balling for *light beers*; 12° to 13° for *draught beers* (Schenkbier); 15° to 20° for *double beers* (Bock or Salvator *beer*); and up to 25° for *table beers*.

beers of a more constant type, since the mother-yeast from successive fermentations does not become contaminated so easily as, and hence requires renewal less frequently than, with top fermentation.[1]

When a large amount of yeast is added to a wort the fermentation is initiated and completed more rapidly; with small quantities the same result is obtained, but after a longer time, so that there is more danger of contamination. Usually 250 to 300 grams of pressed yeast is used per hectolitre of wort—rather more for strong worts.

Especially with top, but also with bottom fermentation, it is most important that all instruments, vessels, and rooms should be kept clean and disinfected. For this purpose, boiling water is used and also dilute solutions of hydrofluoric acid, ammonium fluoride, ammonium fluosilicate, calcium bisulphite, or calcium hypochlorite. In all cases, however, great care must be taken to remove the disinfectant completely with abundant supplies of hot water, in order that the yeast may not be injured. Chloride of lime is eliminated by rinsing first with bisulphite solution and then with hot water. Even traces of bisulphite (sometimes added during mashing to prevent the action of lactic ferments) must be completely eliminated, otherwise, during the *alcoholic fermentation, which is a process of reduction,* they may yield hydrogen sulphide and so give a bad taste and odour to the beer. (Bacteria capable of producing hydrogen sulphide sometimes develop in beer.)

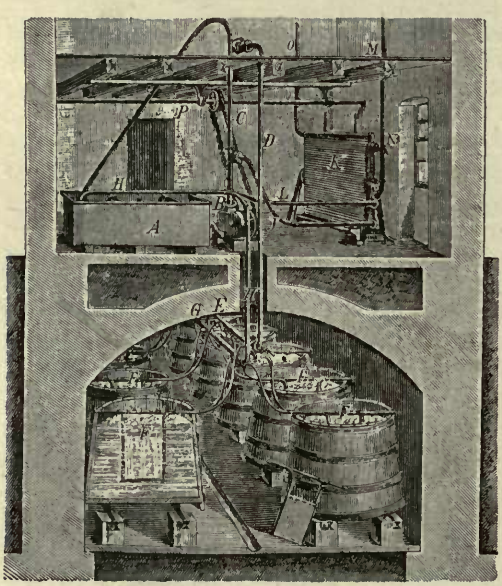

Fig. 169.

The yield and quality of the beer may be improved by adding a pure culture of lactic acid bacteria (preferably Bacillus Delbrücki, *see* p. 152) at the time of *pitching* (*i. e.*, addition of the yeast).

Whatever system of fermentation is used, it is always divided into two phases: the *primary* or *vigorous*, and the *secondary*. The primary fermentation begins twelve or twenty-four hours after pitching, when the yeast has grown to some extent at the expense of the dissolved oxygen, and continues for three or four days in the case of top fermentation or for ten to twelve days with bottom fermentation; considerable quantities of carbon dioxide are developed, these forming a dense, white, frothy head on which may be seen brownish spots of hop resin or agglutinated bacteria. In top fermentation, this first head is removed, the next darker one being collected for pitching purposes.

In the bottom fermentation system, and in large modern breweries in general, in order that the yeast may be kept as pure as possible, the pitching is carried out in the manner described on p. 152 for distilleries.

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[1] With top fermentation, the type and taste of the beer are determined by the united activity of a number of different yeasts and bacteria which are present in given equilibrated proportions, these becoming modified as contamination increases. When the yeast is renewed, the pure yeast naturally gives a different taste to the beer, and this inconvenience cannot be avoided by preparing a mixture of yeasts and bacteria similar to that normally present in the partially contaminated top fermentation. New pure yeasts are less resistant to contaminating surroundings than old ones are.

Attempts are made to-day to keep the fermentation pure as long as possible by the use of good hops, the resins of which exert an agglutinating and paralysing action on the bacteria, so that these can be removed from the tun with the first scum forming on the surface of the fermenting wort; the purer yeast of succeeding heads is then collected for pitching subsequent worts. When the collection of the yeasts is delayed, that of the Frohberg type increases. With the object of maintaining the cultures naturally pure and constant, Effront has proposed the addition of *abietic acid*—a component of *lupulin* and of colophony—to agglutinate and render innocuous the bacteria in fermenting worts (*see also* p. 167). Thus, after elimination of the

During the primary fermentation, a considerable quantity of heat is evolved, and to prevent the temperature exceeding 22° to 25° in top or 7° to 8° in bottom fermentation, *attemperating coils*, through which cold water (top) or brine (bottom) passes, are used to cool the fermenting wort (*F*, Fig. 169). Each fermenting vat is provided with a slate, etc., on which are noted, each day, the temperature and the specific gravity of the wort; the attenuation should reach 58 to 62 per cent. in the primary fermentation and 70 to 75 per cent. in the secondary fermentation, in order that the beers may keep in the warmer rooms of the consumers.[1] When the vigorous fermentation is ended, the head falls and almost disappears, carrying to the bottom of the wort the suspended yeast; in this way the *secondary fermentation* is started, this being allowed to proceed for fifteen to twenty days in the trade casks placed in cellars at 10° to 12° (for top fermentation); the beer is then cleared, filtered, and sold. In bottom fermentation, on the other hand, the secondary fermentation is completed in large tuns pitched inside (*see later*); these are not quite filled

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bacteria with the first scums, purer yeast can be collected and washed with pure water or, better, with water containing a little hydrofluoric acid or ammonium fluoride (5 to 10 grams per hectolitre), which attacks the bacteria, but not the yeast. It cannot, however, be denied that, in general, washing produces considerable weakening of yeast, which may be reinvigorated by preliminary growth in sterilised, unhopped wort.

[1] **Determination of the Attenuation and of the Apparent and Real Extracts of Beer.** The *apparent extract* is deduced from the density of the well-shaken (to remove CO_2) beer and the corresponding number of degrees Balling. The *real extract* is deduced from the specific gravity (and Balling's tables) of the beer freed from alcohol by evaporating it to one-third of its volume and making the residue up to the original volume. The original *extract of the wort* may be calculated with moderate accuracy by adding to the real extract the amount of alcohol (determined as in wine, p. 174) multiplied by 1·92.

The *degree of real attenuation* (*A*) is referred to 1 hectolitre of wort and indicates how many parts per 100 of the *extract* of the wort are transformed into alcohol and carbon dioxide; it is obtained by means of the following formula:

$$A = \frac{D - d}{D} \times 100,$$

where *D* represents the percentage of extract in the wort and *d* the percentage of *real extract of the beer.*

In practice, the percentage of extract is sometimes replaced by the degrees Balling, but the results thus obtained are not very exact. If we make $D = 15°$ Balling and $d = 5°$, the real attenuation becomes:

$$A = \frac{15 - 5}{15} \times 100 = 66{\cdot}66 \text{ per cent.}$$

It cannot, however, be denied that Balling degrees refer to kilos of sugar or of extract in 100 kilos of solution, so that a wort showing 15° Balling (sp. gr. 1·0615) contains 15 kilos of extract per 100 kilos of wort, or 15·922 kilos (*i. e.*, 15 × 1·0615) in a hectolitre of wort; the beer, free from alcohol, showing 5° Balling, has a sp. gr. 1·020, and 1 hectolitre contains 5·100 kilos of extract, so that 10·822 kilos of extract has been fermented and the *true attenuation* is

$$\frac{10{\cdot}822}{15{\cdot}922} \times 10 = 67{\cdot}6 \text{ per cent.}$$

Practical brewers find it more convenient, in considering the degree of attenuation of a wort, to calculate the *degree of apparent attenuation* (*A′*) from the apparent extract of the beer *d* by means of the formula, $A' = \frac{D - d}{D} \times 100$; for example, a wort of 16° Balling has the sp. gr. 1·0658 and 1 hectolitre contains 17·05 kilos of extract, while the beer, with 7° Balling of apparent extract, has the sp. gr. 1·0281, corresponding with 7·20 kilos of extract per hectolitre. The apparent attenuation is hence $\frac{17{\cdot}05 - 7{\cdot}20}{17{\cdot}05} \times 100 = 57{\cdot}9$ per cent.

The attenuation may be deduced in a rather less exact manner if instead of degrees Balling is used degrees of the *legal densimeter* (*i. e.*, the figures in the second decimal place of the specific gravity, a value of 1·063 for the latter thus corresponding with 6·3° on the legal densimeter). In the above example, 16° Balling corresponds with sp. gr. 1·0658, hence with 6·58° on the densimeter; similarly, 7° Balling corresponds with 2·81 densimeter degrees. Hence the apparent attenuation is given by:

$$A' = \frac{6{\cdot}58 - 2{\cdot}81}{6{\cdot}58} \times 100 = 57{\cdot}3 \text{ per cent.},$$

which differs little from the value calculated above from the degrees Balling, and is sufficiently exact for practical purposes. Hence, both for real and apparent attenuation, Balling's tables may be dispensed with, it being sufficient to determine the specific gravity. It should be noted that the legal density expresses the weight of wort contained in the volume occupied by 1 kilo of water measured at 17·5°.

and are kept for one to three months in cellars maintained continually at 0° to 2°, where the beer acquires the desired attentuation and its characteristic flavour. The yeast which is deposited in the fermenting vessels may be collected, pressed (p. 149) and sold to bakers or small brewers.

In some breweries the carbon dioxide is now drawn off from the fermenting vats, which are fitted with covers, by pumps and, after being passed through potassium permanganate solution to purify it, the gas is then liquefied (*see* Vol. I., p. 480); it may be either utilised in the brewery itself or sold.

The fermenting vessels and the storage casks are constructed of oak or pitch-pine. The use of glass vats has been proposed, as these retain the pure flavour of the beer; such a vat to hold 42 hectolitres cost about £40 before the war. The inner walls of the vats are sometimes coated with shellac, paraffin wax or pitch. The cellars have walls and floor of concrete (1 metre higher than the first aqueous border of the subsoil) so that they may be washed when necessary; the roof is of brickwork. These cellars are furnished with draughts to remove the carbon dioxide, with double doors (always on the north side) to prevent the entry of warm air from outside and with electric lighting so that windows, which dissipate the cold, may be avoided. The vats and casks are raised 50 to 60 cm. from the ground and are inclined slightly forward so that they may be emptied completely and easily cleaned from outside. Along the ceiling run pipes for the circulation of cold brine (bottom fermentation), which maintain a temperature below 6° in the fermentation cellars and one of 0° to 2° in the lager cellars.

Ten or fifteen days before the beer is run off from the lager vessels—which have been several times filled up to avoid contact of the beer with the air and consequent danger from acetic ferments—the bung-hole is tightly closed so as to supersaturate the beer under slight pressure with carbon dioxide, which is still developed more or less feebly according to the state of maturity of the beer. If a beer contains, say, 0·15 to 0·25 per cent. of CO_2 before the bung-hole is closed, it will subsequently contain 3 to 8 per cent., which considerably enhances the keeping properties.

Nathan-Bolze Rapid Process (Ger. Pat. 135,539, 1900). This process was tested on an industrial scale in 1904 in the Fermentation Institute at Berlin, and gave satisfactory results. The application of the process has not, however, progressed as rapidly as was hoped for a process which allows of mature beer being prepared in eight to ten days, and works under conditions of sterilisation formerly attainable only in the laboratory or in the manufacture of spirit by the Amylo process (p. 155). The hot, sterile wort from the copper passes into a large, hermetically sealed, sterile vessel of enamelled iron (a special resistant enamel being employed) surrounded by an iron jacket through which water can be passed. These vessels have a capacity of 125 hectolitres or more and are called Hansena vessels. They are provided with powerful stirrers (Fig. 170), which keep the wort in continual motion during the fermentation and thus accelerate the transformation of the maltose into alcohol and carbon dioxide.

After the temperature of the wort has been lowered to 50° by passing water through the jacket and the diminution of pressure (owing to the condensation of steam) compensated by the admission of sterilised air, the latter (which has served also to aerate the wort) is replaced by carbon dioxide, the cooling being continued to 10°. The pure yeast is then introduced through suitable pipes, the mass being slightly stirred at intervals of an hour. The gas developed is removed in order to hasten the fermentation, and is washed with permanganate, part of it then being compressed (*see above*). The carbon dioxide which is not compressed is utilised to remove the *new beer* flavour from beer already fermented in the Hansena vessels; the gas is passed in at the bottom (after removal of the yeast sediment) at the ordinary temperature, the mass being continually stirred meanwhile, it being the carbon dioxide which effects the elimination from the beer of the volatile products to which the disagreeable taste and odour of new beer are due. The gas issues from the top of the vessel, passes to the purifiers and is again conducted through the beer, this process being continued for ten hours on end. The primary fermentation is finished is less than three days, and, after the passage of gas through the beer is completed, the temperature is lowered to 0° and the beer saturated for twenty-four hours with slightly compressed carbon dioxide. The beer is finally filtered and delivered to the trade casks, where it keeps well even in the hot weather.

Such a process, simple, rapid, and economical (the cost of the beer being diminished by about 2*s.* 6*d.* per hectolitre), although it does not give a very delicate flavoured beer, should be suitable to hot countries and to small breweries. Several European breweries already work on these lines, and in 1907 one was constructed at Milan to employ a modification of the Nathan patent, consisting of a system intermediate to the old process with open fermenting vessels and that devised by Nathan; in this case enamelled iron vessels are used both for the primary fermentation and for the maturation (three to four weeks). These vessels cost about £1 for each hectolitre of capacity.

If to the Nathan process is added the Meura system of mashing (1891)—which has rendered the preparation of the wort as simple as possible by mashing the finely ground malt in a horizontal cylinder fitted with stirrers so that the mash may be rapidly cooled or heated and wort ready for passing to the filter-press and thence to the copper obtained in an hour—it will be understood how the manufacture of ordinary beer has been shorn of those practical and theoretical difficulties long regarded as insurmountable.

RACKING OF BEER. Beer is delivered to the consumer in bottles and in casks, and should be perfectly bright, cold, and supersaturated with carbon dioxide. To render it bright, the old method of clarification with gelatine or of filtration through bags has now been largely replaced by the use of the filter-press, which acts more rapidly and yields brilliant beer. The filtration is carried out in suitable frames through filter-cloths or, better, through finely divided cellulose (such as is used in paper-making) under a pressure of about half an atmosphere. These filter-presses are the same in principle as, and little different in form from, those which are used for the filtration of saccharine liquids and are described in the section on Sugar. (In England, beer in cask is clarified by mixing with the beer a small quantity of *finings*, which consist of isinglass "cut" or dissolved in an acid, such as tartaric, sulphurous, etc.; these finings are gradually deposited on the bottom of the cask and carry down with them any suspended protein substances, hop-resins, etc.) Bottling is to-day carried out with all the care employed in the preparation of sparkling wines. A few lines may be devoted to the preparation of beer-casks, since the methods employed are peculiar to the brewing industry.

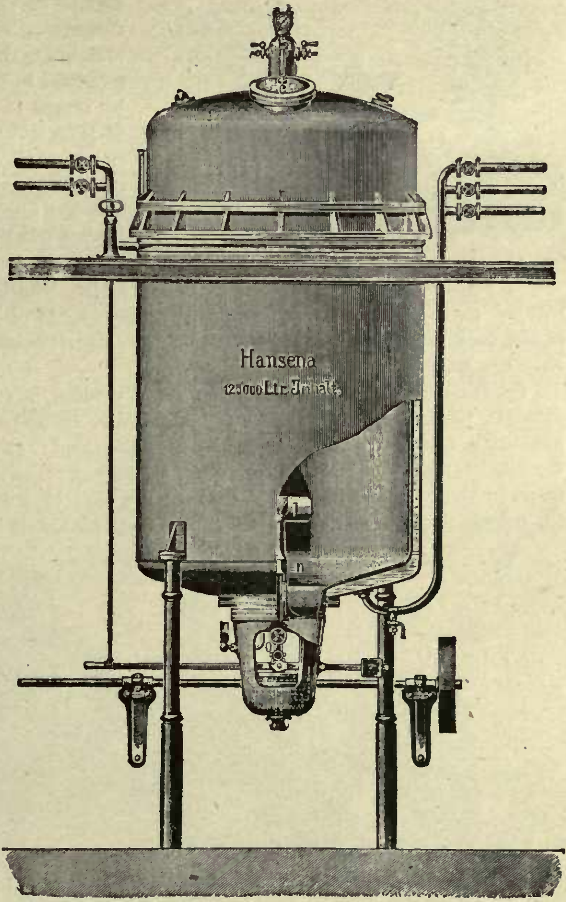

FIG. 170.

In order that beer for retail consumption may retain its flavour, it must be kept cool and saturated with carbon dioxide up to the moment when it is drawn off into the customers' glasses, and for this purpose the use of liquid carbon dioxide with the arrangement shown in Vol. I., p. 483, is well adapted.

RESINING OR PITCHING OF CASKS. The keeping of beer sound depends largely on the cleanliness of its surroundings and of the vessels in which it is stored. Hence the casks, returned empty from the customers, are first well scrubbed and washed both inside and outside with water under pressure by means of automatic plant (Fig. 171), and are then disinfected by means of formalin vapour or other antiseptics, or, better still, by pitching the internal surface with natural or artificial resins, which should be transparent and have a melting-point of about 50°; in this process, which was first used in Bavaria, and is nowadays largely employed all over the Continent, aromatic resins are no longer used, mixtures of colophony with other residues from the distillation of turpentine being prepared by fusion and then rendered more elastic by the addition of resin oil (10 per cent.). Use is sometimes made of a fused mixture containing 50 parts of Burgundy pitch, 20 of stearine, 10 of Japan wax, 10 of paraffin wax, 5 of Venetian turpentine, and 5 of gum dammar. To free the casks from the old resin and coat them again every time they are returned to the brewery, they are heated inside by means of air supplied from a Roots blower, *B* (Fig. 172) and heated by passing through red-hot coke, the hot air being forced into the casks through the tubes, *D*, for five minutes. The old pitch is discharged and the new pitch (about 200 to 250 grams per hectolitre), fused and heated to 250°, introduced into the sterile cask. The bung-hole is then closed, the cask rotated automatically for a few minutes, the excess of pitch poured out, and the rolling of the cask continued until it is cold. The lager-vessels used for the maturation of the beer are treated in a similar way.

FIG. 171.

PASTEURISATION. Beer, more than wine, is subject to numerous changes and diseases (turbidity due to inferior materials, incomplete saccharification or excess of proteins; acidity caused by acetic or lactic acid; stinking fermentation produced by various bacteria, etc.), and it is difficult to remedy these inconveniences except by improvement in the methods of working. In order that beer may remain unchanged when kept for a long time in bottle or when sent to hot places, it is advisable to *pasteurise* it. The bottles are tightly stoppered and placed in vessels containing cold water, which is then *gradually* heated to a maximum of 60° to 65°, this temperature being maintained for ten minutes; the vessels should be covered so as to avoid danger from breakages. The water-bath is subsequently allowed to cool *slowly* to the ordinary temperature. Top-fermentation beers are rarely pasteurised, as they sometimes acquire an unpleasant flavour under this treatment; bottom-fermentation beers, however, undergo no change and keep good even for ten years.

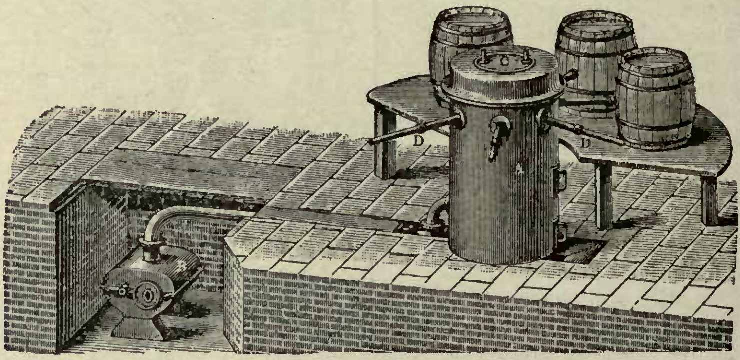

FIG. 172.

In large breweries, very efficient pasteurising apparatus is employed, the bottles being moved automatically in suitable vessels through which the water moves in the opposite direction.

Of the many improved forms in use at the present time, the Gasquet circular type is shown in Fig. 173. Here the chambers are filled successively with baskets of bottles, which are raised by suitable cranes. The water, at a gradually rising temperature, is drawn from each chamber by means of a tube communicating with a pump, heated by a central thermo-syphon, and then passed on to the succeeding chamber. A bell rings every five minutes as a signal for the bottles of a cool chamber to be removed and replaced by fresh ones.

The bottles are made of a special glass, which diminishes the proportion of breakages to less than 1 per cent.

ALCOHOL-FREE BEER. A proposal has recently been made to manufacture beer containing no alcohol by treating wort directly at 0° with yeast which has previously been subjected to special treatment effecting the destruction of almost all the zymase but not that of the peptase and other proteolytic enzymes; the carbohydrates hence give no alcohol, the proteins alone being decomposed. These yeasts remove the flavour of fresh wort, the beer being used before alcoholic fermentation begins (Ger. Pat. 180,128).

COMPOSITION AND ANALYSIS OF BEER. The most varied types of beer are found in different countries, and of each type there are usually the two qualities—*pale* and *dark*.[1] The density varies from 1·010 to 1·030, and the amount of alcohol usually from 3·5 to 4·5 per cent. by volume, although export beers often contain 5 to 5·5 per cent. of alcohol, and certain special

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[1] The compositions of some of the best-known beers are as follow:

	Alcohol	Extract	Ash	Real attenuation
	Per cent. by vol.	Per cent. by vol.	Per cent. by vol.	Per cent. by vol.
Pale Berlin beer	3·91	4·85	0·14	60·50
Berlin lager beer	4·00	6·15	0·20	54·70
Export Bavarian beer	4·78	10·67	0·29	45·44
Munich Spaten beer (at Munich)	3·23	6·61	0·28	48·40
,, ,, ,, (at Milan)	5·23	—	—	—
,, Salvator beer	4·64	9·08	0·28	49·00
,, Spaten table beer	7·0	10·35	—	57·40
,, Bock	4·20	7·10	—	54·20
,, white beer	3·51	4·73	—	59·58
Vienna lager beer	3·62	6·01	—	54·50
Pilsen beer	3·47	4·97	—	59·00
North of France beer	3·20	4·04	—	61·20
Amsterdam beer	4·30	7·0	—	36·40
Brussels lambic	5·94	3·30	—	78·00
Belgian faro	4·33	5·1	—	62·80
Bass's pale ale	6·15	6·87	—	64·00
Scotch pale ale	8·50	10·90	—	59·9
Dublin stout	7·23	6·15	—	70·64
London porter	5·40	6·00	—	63·3
American beer	5·89	6·45	—	63·15
Milan beer: Pilsen type	3·92	5·43	0·21	57·91
,, ,, Munich type	3·50	5·58	0·20	54·63
Porretti beer (Varese)	3·98	5·66	0·22	57·45
Italia beer (made at Milan by the modified Nathan-Bolze process)	4·78	6·00	0·22	59·43

The *real attenuation* (or *degree of fermentation, see* p. 207) is calculated by multiplying the percentage of alcohol by 1·92 (= d'), and adding to this product the extract of the beer, d; this gives the extract, D, contained in the wort prior to fermentation and then the attenuation or percentage of extract fermented $= \frac{D - d}{D} \times 100$.

Some English breweries make **stout** from a mixture of 65 per cent. of pale malt, 10 per cent. of black malt (for colour), 10 per cent. of caramelised malt and sometimes 10 per cent. of cane-sugar and 5 per cent. of maize. This very dark beer is attenuated to a relatively small extent, and retains a full, sweet taste, this being partly due to the almost entire absence of gypsum in, and the small total hardness of, London water; for these beers few hops are used. Export stout is made from worts having gravities as high as 25° Balling, whilst *porter* is lighter in character. The pale beers of Berlin are made with a good proportion (75 per cent.) of malted wheat.

beers still more. The amount of extract also varies considerably, being as much as 12 per cent. for certain types of beer; for ordinary beers it lies between 5 and 6 per cent. (1 per cent. being maltose). The proportion of ash is generally less than 0·3 per cent. The amount of carbon dioxide dissolved varies from 0·15 to 0·40 per cent.

The *analysis of beer* is carried out in a similar manner to that of wine, but the carbon dioxide is eliminated by heating the beer to 40° and shaking for several minutes before the *specific gravity* and *acidity* are determined; the latter does not exceed 0·3 per cent. and is expressed as lactic acid (1 c.c. N/10-alkali ≡ 0·009 gram lactic acid) or as cubic centimetres of normal alkali used per 100 c.c. of beer. To avoid frothing during the distillation of the *alcohol*,[1] a little tannin is added. The *nitrogenous substances* are determined on the extract of 40 c.c. of the beer by Kjeldahl's method (p. 11), the proportion of nitrogen being multiplied by 6·25 to give the corresponding amount of proteins. The reducing sugar is determined by means of Fehling's solution and is calculated as maltose (*see* Note, p. 199).

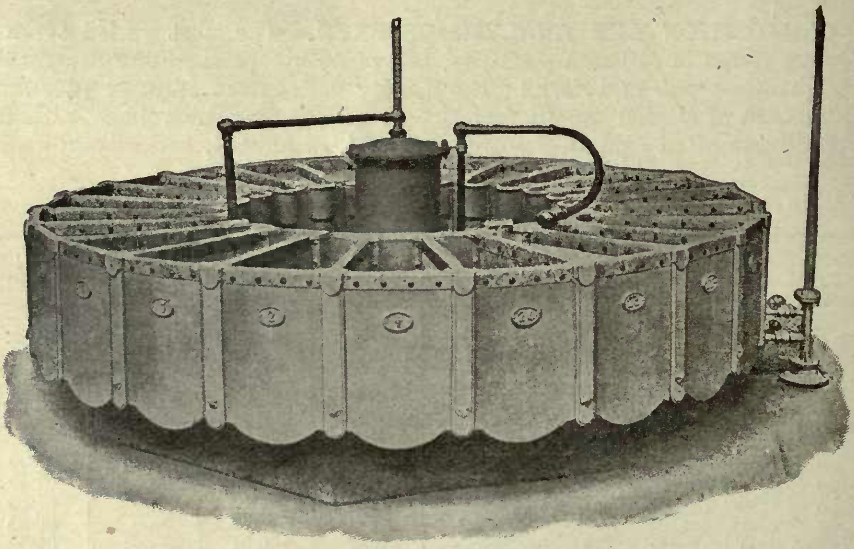

FIG. 173.

Beers are often tested for added salicylic acid, fluorides, sulphurous acid, etc. (*see* Villavecchia's "Applied Analytical Chemistry," Vol. II., p. 164).

STATISTICS. In Italy the brewing industry has never been in a flourishing condition, owing to the abundance and cheapness of wine—possibly more commonly drunk than water. The beer manufactured from remote epochs in Italy was made by the top-fermentation process and was of poor quality; it did not keep well in summer, was stored carelessly by the retailers, and was consumed for only about a couple of months in the year—close to where it was produced. Technical improvements have been introduced tardily, but nowadays the industry is largely concentrated into a few large breweries using the most modern methods and controlled by technical experts from other countries. In 1911 eighty-six breweries were working in Italy.

About one-half of the beer imported into Italy is supplied by Austria-Hungary, about one-third by Germany, and one-tenth by Switzerland:

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[1] The proportion of alcohol may be calculated indirectly by means of the formula, $A = (s/S) \div S$, where A indicates the percentage of alcohol, s the specific gravity of the beer, S the specific gravity of the beer freed from alcohol and made up to the original volume; the alcohol Table (p. 175) gives the percentage by weight corresponding with the value of s/S and division of this percentage by S gives the true percentage of alcohol.

PRODUCTION, IMPORTATION, AND CONSUMPTION OF BEER IN ITALY

	Production hectols.	Imports hectols. in cask.	Consumption	
			Total hectols.	Per head litres.
1880	116,000	46,900	163,000	0·57
1890	160,900	99,500	260,000	0·86
1894–5	95,500	60,000	156,000	0·50
1900	154,000	54,750	209,000	0·66
1903	185,000	70,000	255,000	0·79
1904	220,000	80,000	300,000	0·92
1905–6	304,000	90,000	394,000	1·20
1906–7	360,000	94,494	455,000	1·50
1907–8	400,000	95,213	495,000	1·60
1908–9	473,000	88,100	561,000	1·80
1909–10	563,000	89,737	651,000	2·00
1910–11	598,000	83,365	680,000	2·10
1911–12	721,000	97,700	815,000	2·40
1912–13	673,000	90,000	763,000	2·30
1913–14	652,300	66,000	718,000	2·20
1914–15	526,000	12,000	538,000	1·70

The consumption of beer in Italy takes place mostly in the towns of the north and centre, and the average consumption per head in Milan, Turin, or Rome is at least ten times that for the whole country.

The production and consumption of beer in different countries are as follows (thousands of hectolitres):

	1881	1900	1905	1908	1910	1913	Mean consumption per head (litres)
Germany	35,000	67,000	66,000	69,500	64,000	68,000	118 (1909) 101 (1910)
Austria-Hungary	12,000	20,000	—	20,400	19,000	25,000	80 ,,
Great Britain	45,000	59,000	—	59,000	58,000	60,667	153 ,,
Belgium	9,000	14,000	—	14,000	16,000	16,000	211 ,,
France	8,000	9,000	13,700	—	14,000	16,000	32 ,,
United States	19,000	48,000	—	64,000	70,000	73,000	63 ,,
Russia	7,000	—	6,500	—	6,200	11,500	5 ,,
Spain	—	1,000	—	—	—	400	—
Switzerland	1,000	—	—	—	1,500	3,000	—
Holland	—	—	—	—	—	1,800	38 ,,
Norway	—	—	—	—	—	500	31 ,,
Sweden	—	—	—	—	—	2,850	56 ,,
Denmark	—	—	—	—	—	350	104 ,,
Japan	—	—	—	294	280	354	—
New Zealand	—	—	—	—	2,456	—	—
Argentine, Chili, Brazil	—	—	—	—	2,241	1,100	—
Whole world	—	—	—	—	271,000	275,000	—

In Northern Germany the mean annual consumption per head was only 98 litres, whereas in the Grand Duchy of Baden it amounted to 158 litres; for Lille the quantity was 360 litres.

Delbrück calculated that in 1911 almost £160,000,000 was invested in breweries throughout the world, barley to the value of £14,400,000 and hops to the value of £1,600,000 being used in the brewing of beer.

In 1900 the breweries in Germany numbered 10,000. In 1909 Bavaria produced 18,000,000 hectolitres of beer, Wurtemberg 5,500,000, Baden 3,000,000, and North Germany 38,000,000.

In 1911 the Schultheiss Brewery of Berlin made 1,500,000 hectolitres of beer and the Dreher Brewery of Schwechat (Vienna) 1,100,000 hectolitres.

A large brewery near New York produces annually 900,000 barrels of beer, its ice machines having a daily capacity of 1600 tons.

The brewery of Guinness & Co., Dublin, makes about 3,500,000 hectolitres of stout per year.

In Italy the brewing tax was 5¾*d.* up to 1891, when it was raised to 11½*d.* (causing a temporary diminution in the consumption at that time) per saccharometer degree per hectolitre, measured with the decimal saccharometer at 17·5° on the wort from the *cooler*, an allowance of 12 per cent. being made for loss during the subsequent operations; the tax varied from a minimum of 9*s.* 6*d.* to a maximum of 15*s.* 4*d.* per hectolitre, according to the strength of the beer. Imported beer pays 2*s.* 5*d.* more, or the importers can demand the tax to be levied on the extract degrees, these being increased by twice the number of alcohol degrees. On exported beer the duty is refunded to the extent of 9*s.* 6*d.* per hectolitre. The exchequer collected £180,000 in 1905–1906, £211,800 in 1906–1907, and £320,000 in 1910–1911 as tax of manufacture. During the war the duty was raised to 1*s.* 5*d.* per hectolitre-degree, and it is proposed to increase it to 2*s.* 5*d.* in 1920.

In Germany beer costs about 12*s.* per hectolitre, or rather more with the extra taxation of 1910. In Italy the cost is about 32*s.* (that imported from well-known breweries about 40*s.* per hectolitre).

VARIOUS DERIVATIVES OF ETHYL ALCOHOL

SODIUM ETHOXIDE, $C_2H_5{\cdot}ONa$, may be obtained by dissolving metallic sodium in absolute alcohol: $C_2H_5{\cdot}OH + Na = C_2H_5{\cdot}ONa + H$; when the dense mass is cooled, the crystallised ethoxide separates with $3C_2H_5{\cdot}OH$, which it loses only when heated to 200° in a current of hydrogen, a soft white powder remaining. The latter separates directly when the calculated quantity of sodium is dissolved in absolute alcohol previously dissolved in ether or toluene and heated in a reflux apparatus. The ethoxide is also obtained when sodium hydroxide is dissolved in concentrated alcohol. With excess of water sodium ethoxide decomposes into alcohol and caustic soda.

The ethoxide is largely used in organic syntheses and to remove water and alcohol; before the war it cost 28*s.* to 32*s.* per kilo.

CALCIUM ETHOXIDE $(C_2H_5O)_2Ca$, is formed on dissolving metallic calcium in alcohol or by heating calcium carbide with absolute alcohol.

ALCOHOLS HIGHER THAN ETHYL ALCOHOL

PROPYL ALCOHOLS, C_3H_8O. The two isomerides theoretically possible are known:

(1) **Normal,** $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ (*propanol*-1 or *ethylcarbinol*). This may be obtained from fusel oil (p. 165) by fractional distillation, or from its bromo-derivative, or by the action of magnesium ethyl chloride on trioxymethylene. It has an agreeable odour, b.-pt. 97°, sp. gr. 0·804, and is readily soluble in water, but insoluble in cold saturated calcium chloride solution (unlike ethyl alcohol). On oxidation it gives propionic acid, which proves its constitution.

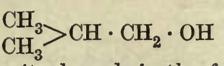
(2) **Sec. Iso-Propyl Alcohol,** $CH_3 \cdot CH(OH) \cdot CH_3$ (*propanol*-2 or *dimethylcarbinol*), is a colourless liquid, b.-pt. 81°, sp. gr. 0·789. It is obtained from isopropyl iodide and hence indirectly from glycerol, or by reducing acetone with sodium amalgam, the constitution attributed to it being thereby confirmed.

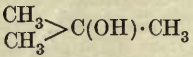
BUTYL ALCOHOLS, $C_4H_{10}O$. The four isomerides, predicted by theory, are known:

(1) **Normal Butyl Alcohol,** $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ (*butanol*-1 or *propylcarbinol*), is a liquid, b.-pt. 117°, sp. gr. 0·810, and has an irritating odour; 12 vols. of water at 22° dissolve only 1 vol. of it, this being separated from the solution by the addition of a soluble salt. It is found in fusel oil and may be obtained by fermenting glycerol or mannitol (yield 8 to 10 per cent.) with *Bacillus butylicus* (contained in the excreta of cows). It may also be prepared synthetically by the various general processes (p. 125). Its constitution is indicated by its syntheses and by the possibility of transforming it into normal butyric acid by oxidation.

(2) **Secondary Butyl Alcohol,** $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_3$ (*butanol*-2 or *ethylmethylcarbinol*), is a liquid with an intense, peculiar odour, b.-pt. 100°, sp. gr. 0·808. It may be

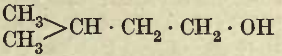
obtained by treating the tetrahydric alcohol, erythritol, $C_4H_6(OH)_4$, with hydriodic acid or by the interaction of normal butylene and hydriodic acid and hydrolysis of the resulting iodide.

(3) Isobutyl Alcohol,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot OH$ (*methylpropanol*), is termed also *butyl alcohol of fermentation*, since it abounds in the *fusel oil of potatoes*, from which it may be extracted by forming the corresponding iodo-compound. It is a colourless liquid, b.-pt. 107°, sp. gr. 0·806, and has a characteristic alcoholic smell. Its constitution is determined by the fact that, on oxidation, it yields isobutyric acid, the constitution of which is known.

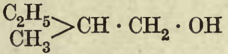
(4) Tertiary Butyl Alcohol,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C(OH)\cdot CH_3$ (*trimethylcarbinol* or *methyl-2-propanol*), occurs in small proportion in fusel oil, and may be prepared by the action of hot 75 per cent. sulphuric acid on isobutylene, which thus takes up 1 mol. of water. When pure, it forms rhombic prisms or plates, m.-pt. 25·5°, sp. gr. 0·786 (solid), b.-pt. 83°. On oxidation it gives acetic acid, acetone, and carbon dioxide.

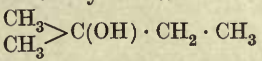
AMYL ALCOHOLS, $C_5H_{11}\cdot OH$. The eight isomerides theoretically possible are known, the most important being:

(1) Normal Amyl Alcohol, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ (*pentanol*-1), b.-pt. 138°, sp. gr. 0·817, is of little importance, and is obtained by reducing normal valeraldehyde or by the other general methods.

(2) Amyl Alcohol of Fermentation,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot CH_2\cdot OH$ (*methyl*-3-*butanol*-1 or *isobutylcarbinol*), is a liquid, b.-pt. 131°, sp. gr. 0·810, and is solid at — 134°. It dissolves in 50 vols. of water at 13·5°, but in presence of a little ethyl alcohol its solubility is greatly increased. It has a higher bactericidal action than other alcohols, and, owing to its toxicity, great precautions are taken in its manufacture to protect the health of the workpeople; if it could be obtained at a low price, it might be used for making isoprene and hence synthetic rubber. It imparts its characteristic smell and burning taste to fusel oil, in which it abounds. It is to this alcohol that the poisoning effect of spirits is principally due. It occurs naturally in Roman chamomile oil and is obtained industrially from fusel oil (*see* note, p. 165). It is used in large quantities to prepare amyl acetate, which serves as an excellent solvent for cellulose acetate. Prior to the war it cost £80 to £120 per ton.

In 1911 the United States produced 250 tons. Germany exported 82 tons in 1910, 56 in 1911, and 124 in 1912, and imported 2·7 tons in 1910, 36 in 1911, and 197 in 1912.

(3) Active Amyl Alcohol,  $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot OH$ (*methyl*-2-*butanol*-1 or 2-*methylbutan*-1-*ol*), boils at 128°, has the sp. gr. 0·816, and is found with the amyl alcohol of fermentation. It contains an asymmetric carbon atom (*see* p. 19) and is lævo-rotatory, whilst the halogen compounds and the valeric acid derived from it are dextro-rotatory; also the dextro-isomeride of this acid yields a lævo-rotatory iodide.

(4) Tertiary Amyl Alcohol,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C(OH)\cdot CH_2\cdot CH_3$ (*methyl*-2-*butanol*-2 or *amylene hydrate* or *dimethylethylcarbinol*) is an oily liquid with a faint odour of mint. It boils at 102° and is prepared from amylene by the indirect addition of water under the influence of sulphuric acid. It exerts a soporific effect.

HIGHER ALCOHOLS. Of these may be mentioned: *Primary normal hexyl alcohol* or *hexanol*, $CH_3\cdot[CH_2]_4\cdot CH_2\cdot OH$ (14 of the 18 hexyl alcohols predicted by theory are known), which may be obtained from caproic acid, $C_6H_{12}O_2$, and is found as butyric and acetic esters in the ethereal oil of the seeds of *Heracleum giganteum* and in the fruit of *Heracleum spondylium*: it boils at 158° (under 740 mm. pressure), and has the specific gravity 0·820. *Caproyl* or *isohexyl alcohol*, $(CH_3)_2:CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, b.-pt. 150°, is found in vinasse and in fusel oil. *Heptyl* (or *œnanthyl*) *alcohol*, $C_7H_{16}O$; of the 38 possible isomerides, 13 are known. *Normal octyl alcohol*, $C_8H_{18}O$, is contained in *Heracleum spondylium* and *Heracleum giganteum*; *secondary octyl alcohol* (or *capryl alcohol* or *methylhexylcarbinol*) is formed on distilling castor-oil. Other higher alcohols are obtained by reducing the corresponding aldehydes with zinc dust and acetic acid; they are solid, like paraffin wax. *Cetyl* or *normal hexadecyl alcohol*, $C_{16}H_{34}O$, combined with palmitic acid, forms the principal component of sperm oil. *Ceryl alcohol* (*cerotin*), $C_{26}H_{53}\cdot OH$, occurs as cerotic ester in Chinese wax and in wool-fat; it melts at 76° to 79°. *Melissyl* or *myricyl alcohol*, $C_{30}H_{61} \cdot OH$ (?), is found as the palmitic ester in beeswax and carnauba wax, and is obtained free by saponification with alcoholic potash.

II. UNSATURATED MONOHYDRIC ALCOHOLS

These are similar to the saturated alcohols, but, as they contain one or two double linkings, they behave like the olefines and diolefines in taking up two or four atoms of hydrogen, halogens, etc., to give saturated compounds. If they contain a triple linking, $—C \equiv CH$, they form explosive metallic compounds, as does acetylene (p. 110).

VINYL ALCOHOL, $CH_2 : CH . OH$ (Ethenol), appears to be present in commercial ether, but it has never been isolated, attempts to synthesise it leading, as is the case with other similar compounds, to an isomeride—acetaldehyde, $CH_3 \cdot CHO$; the formation of the latter is explained by the addition of a molecule of water to the alcohol, and immediate loss of a molecule of water from the compound thus formed.

ALLYL ALCOHOL, $CH_2 : CH \cdot CH_2 \cdot OH$ (Propenol), is a liquid of pungent odour, density 0·8573 at 15°, b.-pt. 98°, and readily soluble in water. It is formed in small quantity in the distillation of wood (crude methyl alcohol contains 0·2 per cent., and the final products of the rectification, distilling at 80° to 100°, 50 per cent. of it). Industrially it is obtained by heating glycerol (4 parts) with crystallised oxalic acid (1 part) or formic acid and 0·3 per cent. of ammonium chloride; below 130° CO_2 is evolved with formation of glycerol formic ester, $CH_2(OH) \cdot CH(OH) \cdot CH_2 \cdot COOH$, which begins to decompose at 205° to 210° and is completely decomposed at 260°, with evolution of CO_2 and H_2O. The crude allyl alcohol is distilled off (at 195° to 200°) and is redistilled until oil no longer separates, when a small portion of the distillate is treated with potash. From the distillate the allyl alcohol is obtained as an oil by addition of potash, the oil being decanted off, dried by prolonged contact with lump caustic potash, again distilled and dried over potassium carbonate which has been recently heated and then over baryta. The yield is 22 to 25 per cent. of the weight of oxalic acid taken.

Cl, Br, CN, and HClO can be added on to it directly, but not H. When cautiously oxidised, it takes up O and H_2O, giving glycerol or even acroleïn (allyl aldehyde) and acrylic acid, which shows it to be a primary alcohol.

It is used to prepare allyl bromide and iodide (*see below*), esters of salicylic and cinnamic acids, etc. The price of the alcohol is 28*s.* to 32*s.* per kilo, the chemically pure product costing twice as much.

Derivatives of allyl alcohol occur in the vegetable kingdom. Thus oil of garlic contains diallyl disulphide and triallyl trisulphide, and mustard oil, allyl thiocyanate (or allylthiocarbimide), $C_3H_5 \cdot N : C : S$. Mustard oil is obtained from pressed mustard oil seeds (which contain it as the glucoside of potassium myronate, this being easily decomposed by the enzyme myrosin), and is also prepared artificially by distilling allyl iodide with potassium thiocyanate. The natural product (containing 94 per cent. of allyl isothiocyanate) cost before the war £2 per kilo and the artificial oil 12*s.* per kilo. It is used for preparing mustard compounds and serves as a vesicatory, etc.

CITRONELLOL, $C_{10}H_{20}O$, is found in attar of roses.

PROPARGYL ALCOHOL, $CH \vdots C \cdot CH_2 \cdot OH$ (Propinol), is a liquid with a pleasant odour, lighter than water, b.-pt. 114°.

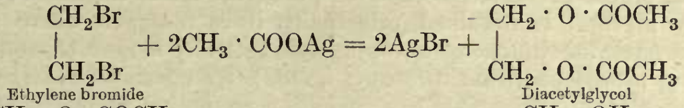
GERANIOL, $C_{10}H_{18}O$ or $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CH_2 \cdot OH$, is a pleasant-smelling oil, b.-pt. 121° under 17 mm. pressure. It is obtained from geranium oil, and on oxidation gives *citral* (the corresponding aldehyde) which occurs in mandarin oil and in essences of orange and lemon and to a very considerable extent (60 per cent.) in verbena oil.

III. POLYHYDRIC ALCOHOLS

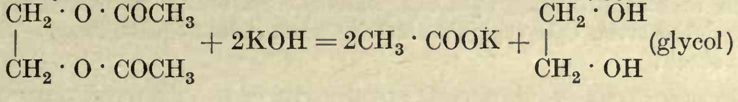
(*a*) DIHYDRIC ALCOHOLS OR GLYCOLS, $C_nH_{2n}(OH)_2$

Substitution of two hydrogen atoms, joined to different carbon atoms, by two hydroxyl groups gives dihydric alcohols, containing two alcoholic groups. It is not, however, possible to have two hydroxyl groups united to the same carbon atom—although similar compounds are known for the ether derivatives known as Acetals (*see later*)—since even if they could be formed they would immediately lose a molecule of water, forming aldehydes or ketones.

The dihydric alcohols, owing to their sweet taste, were called **Glycols** by Wurtz, who prepared them by transforming a dihalogenated hydrocarbon into the corresponding diacetyl-ester by means of silver acetate and then saponifying the diacetyl compound either by baryta or sodium hydroxide or by boiling with water and lead oxide or sodium carbonate solution :

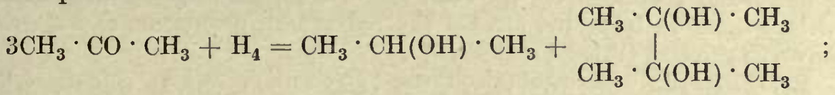


$$\underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}} + 2CH_3\cdot COOAg = 2AgBr + \underset{\text{Diacetylglycol}}{\begin{array}{l}CH_2\cdot O\cdot COCH_3\\ |\\ CH_2\cdot O\cdot COCH_3\end{array}}$$



$$\begin{array}{l}CH_2\cdot O\cdot COCH_3\\ |\\ CH_2\cdot O\cdot COCH_3\end{array} + 2KOH = 2CH_3\cdot COOK + \begin{array}{l}CH_2\cdot OH\\ |\\ CH_2\cdot OH\end{array}\quad\text{(glycol)}$$

A special group of glycols, the *pinacones*, containing two adjacent tertiary alcohol groups ($\equiv C\cdot OH$), are formed by reducing the ketones with sodium and water, or, better, together with isopropyl alcohol, by electrolysing a dilute solution of sulphuric acid and acetone, the latter being reduced at the negative pole :



$$3CH_3\cdot CO\cdot CH_3 + H_4 = CH_3\cdot CH(OH)\cdot CH_3 + \begin{array}{c}CH_3\cdot C(OH)\cdot CH_3\\ |\\ CH_3\cdot C(OH)\cdot CH_3\end{array};$$

this *pinacone* (2 : 3-dimethyl-2 : 3-butandiol), melts at 38°, boils at 172° and crystallises with $6H_2O$. When distilled with dilute sulphuric acid, it is transformed into *pinacoline*, $(CH_3)_3C\cdot CO\cdot CH_3$, with separation of H_2O and transposition of an alkyl group.

The glycols have an almost oily appearance ; their solubility and sweetness increase with the molecular weight, while the specific gravity and boiling-point are much higher than those of the monohydric alcohols with equal numbers of carbon atoms. The hydroxyl groups of the glycols behave like those of monohydric alcohols, so that the glycols can give rise to ethers and esters, alkoxides (sodium, etc.), halogen compounds (*e. g.*, the *chlorohydrins*), aldehydes and acids, besides which they may give up 1 mol. of H_2O forming anhydrides.

ETHYLENE GLYCOL (Ethan-1 : 2-diol), $C_2H_4(OH)_2$, is a dense liquid, b.-pt. 198°, and, on oxidation, yields glycollic acid, $CO_2H\cdot CH_2\cdot OH$ and oxalic acid, $CO_2H\cdot CO_2H$.

PROPYLENE GLYCOLS. Two isomerides are known : **α-Propylene Glycol**, $OH\cdot CH_2\cdot CH(OH)\cdot CH_3$ (*propan-1 : 2-diol*), boils at 188° and is formed on distillation of glycerol with sodium hydroxide. It contains an asymmetric carbon atom and, by the action of certain ferments, the lævo-rotatory isomeride may be isolated. **β-Propylene Glycol** boils at 216° and is formed by the bacterial decomposition of glycerol, as well as by the usual synthetical methods.

In the higher glycols, when the two hydroxyl groups have four carbon atoms between them (γ-glycols), water is readily separated and furan derivatives, analogous with pyrrole and thiophene compounds, formed.

(*b*) TRIHYDRIC ALCOHOLS, $C_nH_{2n-1}(OH)_3$

These are colourless, dense liquids with a sweetish taste and readily soluble in water ; they contain at least three carbon atoms and three hydroxyl groups, and are hence capable of forming three series of esters by combination with a monobasic acid.

GLYCEROL (or *Glycerine*), $C_3H_5(OH)_3$, or $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ (**Propantriol**), was discovered by Scheele in 1779. Chevreul and Braconnot

(1817) found it as a component of all oils and fats. Its formula and constitution were established later (Pelouze, Wurtz, and Berthelot). It occurs abundantly in nature, not in the free state, but combined with higher fatty acids in the form of esters (*glycerides*), which form the fats and oils; these contain 9 to 11 per cent. of combined glycerol.

It exists free in rancid fats and is formed in small proportions in the fermentation of sugar (all wines contain 0·98 to 1·67 per cent.).

During the European War glycerol was prepared in Germany to some extent by biological processes and was sold in the pure state under the name of *protol.*[1] Industrially glycerol is obtained principally from factories where fats are decomposed (stearine- and soap-works). Synthetically it may be obtained by transforming propylene (from isopropyl iodide), by means of chlorine in the hot, into dichloropropane, $C_3H_6Cl_2$, which, with iodine chloride, gives the trichloro-derivative, $C_3H_5Cl_3$; the latter, when heated with water at 170°, gives glycerol:

$$CH_2Cl \cdot CHCl \cdot CH_2Cl + 3H_2O = 3HCl + OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH.$$

This formation of glycerol and also that by the oxidation of allyl alcohol, $CH_2 \cdot CH \cdot CH_2 \cdot OH$, demonstrate the constitution of glycerol. On the other hand, it is possible to prepare glycerol synthetically from the elements by way of acetylene, acetaldehyde (p. 110), acetic acid, acetone (by distillation of calcium acetate), isopropyl alcohol (by reduction), propylene, and thence, as above, to glycerol (Friedel and Silva).

PROPERTIES. Glycerol (also termed glycerine) is an oily, colourless, dense liquid of sp. gr. 1·2641 at 15°, and $1{\cdot}26413 + (15 - t)\ 0{\cdot}000632$ at any other temperature, t. It is highly hygroscopic when concentrated, but this property is no longer shown when the glycerol contains 20 per cent. of water. It dissolves in water and in alcohol in all proportions, heat being generated when 58 parts of glycerol are mixed with 42 parts of water. Glycerol has a sweet taste.

It is insoluble in ether or chloroform; it dissolves to the extent of 5 per cent. in dry acetone and to a greater degree in aqueous acetone. It boils at 290° with partial decomposition, but it may be distilled unchanged in a vacuum (at 10 mm. pressure it boils at 162°). It crystallises at − 40° or at a higher temperature if it contains water; the separated crystals melt only at 22°.

When heated for a long time at 130° to 160° in presence of sulphuric acid, glycerol loses one or more molecules of water, giving anhydrides or ethers of glycerol or *polyglycerines* (A. Nobel, 1890); W. Will (1904) arrived at the same result by heating glycerol for seven to nine hours at 290° to 295° and distilling off the water formed. This treatment yields about 60 per cent. of *diglycerine*, $C_3H_5(OH)_2 \cdot O \cdot C_3H_5(OH)_2$, and a little tri- and polyglycerines; all these products may be esterified like glycerol and yield, *e. g.*, *tetranitrodiglycerine*, which does not congeal even at −20° and has an explosive power like trinitro-

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[1] The process used appears to be that of Connstein and Lüdecke, based on the observation that the amount of alcohol formed during fermentation diminishes and that of glycerol formed increases as sodium sulphite is added to the saccharine liquid in increasing proportions. The results obtained with a 10 per cent. sugar solution containing also small amounts of ammonium sulphate, sodium phosphate, and potassium salts, are illustrated by the following figures:

Sulphite employed	25	50	100
Glycerol formed	113	196	271
Alcohol ,,	400	287	233
Aldehyde ,,	24	58	86
Carbon dioxide formed	396	358	294

When the fermentation is finished, the yeast (recoverable) is removed by filtration and the aldehyde and alcohol by distillation. From the residual liquid salts and acids are separated by means of calcium chloride and excess of the latter by sodium carbonate, the liquid being filtered and concentrated; glycerol slightly contaminated with glycol is thus obtained.

glycerine (*see also* C. Claessen, Ger. Pats. 181,754 and 198,768, 1907). According to U.S. Pats. 978,443 (1910) and 13,234 (1911), glycerol readily polymerises when heated at 275° in presence of 0·5 to 1·0 per cent. of sodium acetate, 70 per cent. being polymerised in an hour.

When heated rapidly and strongly it decomposes, yielding partly acroleïn with the characteristic pungent odour. Also when heated with P_2O_5 or $KHSO_4$, it loses $2H_2O$, giving acroleïn, $CH_2 : CH \cdot CHO$.

One hundred parts of glycerol dissolve the following quantities of mineral salts: 98 of sodium carbonate, 60 of borax, 50 of zinc chloride, 40 of potassium iodide, 10 of boric acid, 50 of tannin; bromine, ammonia, ferric chloride, etc., are also dissolved.

Glycerol has the refractive index 1·476 at 13° and in aqueous solution the index varies proportionally with the dilution. By means of Lenz's table, the concentration of glycerol solutions may be determined from either the specific gravity or the index of refraction:

Percentage of glycerol	Degrees Baumé, Beck, Gerlach	Sp. gr. at 12° to 14°	Index of refraction at 12·5° to 12·8°	Percentage of glycerol	Degrees Baumé, Beck, Gerlach	Sp. gr. at 12° to 14°	Index of refraction at 12·5° to 12·8°
100	30·7	1·2691	1·4758	54	18·0	1·1430	1·4065
99	30·4	1·2664	1·4744	52	17·4	1·1375	1·4036
98	30·1	1·2637	1·4729	50	16·9	1·1320	1·4007
97	29·8	1·2610	1·4715	48	16·2	1·1265	1·3979
96	29·6	1·2584	1·4700	46	15·5	1·1210	1·3950
95	29·4	1·2557	1·4686	44	15·0	1·1155	1·3921
94	29·1	1·2531	1·4671	42	14·3	1·1100	1·3890
93	28·9	1·2504	1·4657	40	13·6	1·1045	1·3860
92	28·7	1·2478	1·4642	38	13·0	1·0989	1·3829
91	28·5	1·2451	1·4628	36	12·3	1·0934	1·3798
90	28·2	1·2425	1·4613	34	11·5	1·0880	1·3772
88	27·7	1·2372	1·4584	32	11·0	1·0825	1·3745
86	27·1	1·2318	1·4555	30	10·3	1·0771	1·3719
84	26·6	1·2265	1·4525	28	9·6	1·0716	1·3692
82	26·1	1·2212	1·4496	26	9·0	1·0663	1·3666
80	25·6	1·2159	1·4467	24	8·3	1·0608	1·3639
78	25·1	1·2106	1·4438	22	7·6	1·0553	1·3612
76	24·5	1·2042	1·4409	20	6·9	1·0498	1·3585
74	24·0	1·1999	1·4380	18	6·1	1·0446	1·3559
72	23·5	1·1945	1·4352	16	5·6	1·0398	1·3533
70	23·0	1·1889	1·4321	14	4·9	1·0349	1·3507
68	22·3	1·1826	1·4286	12	3·8	1·0297	1·3480
66	21·6	1·1764	1·4249	10	3·4	1·0245	1·3454
64	21·0	1·1702	1·4213	8	2·8	1·0196	1·3430
62	20·3	1·1640	1·4176	6	2·1	1·0147	1·3405
60	19·8	1·1582	1·4140	4	1·3	1·0098	1·3380
58	19·2	1·1530	1·4114	2	0·7	1·0049	1·3355
56	18·6	1·1480	1·4091				

The specific gravity may be corrected for the temperature by adding or subtracting 0·7 per cent. for each degree above or below 15°.

The specific viscosity (p. 90) varies greatly with the water-content.

Glycerol has the interesting property of preventing the precipitation of various metallic hydroxides (*i. e.*, it keeps them dissolved); for instance, in presence of glycerol, potassium hydroxide does not precipitate salts of chromium, copper, etc. With alkalis it forms slightly stable soluble alkoxides. It does not reduce silver or cupric salts, and hence cannot contain aldehyde groups;

it is not coloured by concentrated sulphuric acid or by sodium hydroxide on boiling. The halogens act on glycerol, not as substituting, but as oxidising agents. It inverts cane-sugar and renders starch soluble; 100 parts of glycerol and six of starch at 190° give *starch soluble* in water, and the starch may be separated from the glycerol, when cold, by precipitation with alcohol.

Like the other polyhydric alcohols (glycols, erythritol and its isomerides, also glucose and its isomerides—galactose, etc.—but not cane-sugar, quercitol or dextrin) glycerol, when added in sufficient quantity, transforms the alkaline reaction of borax solutions into an acid reaction, thus allowing of the determination of boric acid and borax by titration.

Under the action of certain schizomycetes, glycerol yields normal butyl alcohol, butyric acid and, partly, ethyl alcohol.

Being a trihydric alcohol, glycerol is able to form esters of three types (mono-, di- and tri-), according as one, two, or three hydroxyl groups are replaced by inorganic or organic acid residues. In this way the glycerides may be regenerated; for example, when excess of stearic acid is heated with glycerol at 200° under reduced pressure until no more water separates, *tristearin* is formed.

When cautiously oxidised, glycerol forms first *glyceric acid*, $OH \cdot CH_2 \cdot CH(OH) \cdot COOH$, which undergoes further oxidation to *tartronic acid*, $COOH \cdot CH(OH) \cdot COOH$, so that it is proved that glycerol contains two primary alcohol groups ($\cdot CH_2 \cdot OH$); also, as tartronic acid still exhibits alcoholic characters, it must contain a secondary alcohol group. The constitution of glycerol is hence completely proved.

USES OF GLYCEROL. The bulk of the glycerol manufactured is used for the preparation of nitroglycerine and hence of dynamite (*see later*); to some extent it serves for the manufacture of glycerinacetin, which is employed in making explosives and in printing textiles. It is also used to give body to light wines (termed *Scheelisation*, after Scheele, the discoverer of glycerol). It is employed in the manufacture of liqueurs, syrups, preserves, and sweetmeats, since it is sweet and dense, and, to some extent, anti-fermentative. It is added to chocolate, tobacco, cosmetics, textiles to be dressed, and leather goods, since it does not dry and keeps them soft or pliable. It is also used in extracting from flowers and herbs delicate perfumes which would undergo change if extracted by distillation.

It is employed as a non-congealing and lubricating liquid (a solution of sp. gr. 1·13) in gas-meters and in hydraulic pumps; for greasing iron objects to prevent them from rusting; for making copying-ink, soap, and shoe-polish; for preserving anatomical preparations, etc.

INDUSTRIAL PREPARATION. Glycerol is obtained almost exclusively as a secondary product in the treatment of fats. Until the year 1885 only the aqueous residues of stearine works were worked up (the fats are decomposed with lime, sulphuric acid, steam, or ferments), but nowadays almost all the alkaline lyes of soap factories (where the fats are treated directly with caustic soda and then with salt) [1] are utilised.

Of the 9 to 11 per cent. of glycerol contained in fats, 8 to 10 per cent. may be recovered (only 4 per cent. when the decomposition is effected by sulphuric acid, the maximum yield being obtained when water or enzymes are used).

The treatment of the dilute solutions of crude glycerol varies with their origin: soap-lyes (which are sometimes concentrated in the soap-works and sold to the glycerol refiners) are treated with 0·1 to 0·2 per cent. of lime or ferrous sulphate and mixed by means of an air-jet; the liquid is decanted, slightly acidified with hydrochloric acid and skimmed; a small quantity of aluminium sulphate is then added, the liquid being decanted, rendered

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[1] These lyes have an alkaline reaction and, on analysis, one of them (somewhat dense) gave the following results: water, 61 per cent.; glycerol, 16·5 per cent.; salts, 22 per cent. (eight-tenths of which were NaCl, one-tenth Na_2SO_4, and one-tenth Na_2CO_3). The specific gravity varies from 3° to 7° Bé., and the proportion of glycerol usually from 6 to 12 per cent.

slightly alkaline, passed through a filter-press and concentrated in open boilers furnished with stirrers until sodium chloride begins to separate; subsequent concentration to the sp. gr. 28° Bé. is carried out in a vacuum, the salt deposited being gradually removed. This *crude glycerol* contains 85 to 90 per cent. of glycerol and 1 per cent. of salts, and has a dark yellow or brownish colour. Sometimes the alkali is removed from the soap lyes by adding a little resin and boiling, so that the resin soap formed is carried to the surface and may be decanted (to be utilised by adding to ordinary soap).

The free lime may also be precipitated with an oxalate or with carbon dioxide and the sulphates with barium chloride. The concentration is not carried out in open vessels, as, when the aqueous solutions are vigorously boiled, the steam given off carries away appreciable quantities of glycerol. The concentration is hence carried to a certain point in an apparatus (Fig. 174 shows the Droux apparatus and Fig. 175 that of Morane), fitted with rotating coils or hollow lenticular discs, in which steam under pressure circulates. The apparatus is covered in and the steam from the solution issues rapidly through a tube communicating with an aspirator. When the density reaches 18° to 20° Bé. the solution is decanted or filtered and then further concentrated in a vacuum to 27° to 28° Bé.

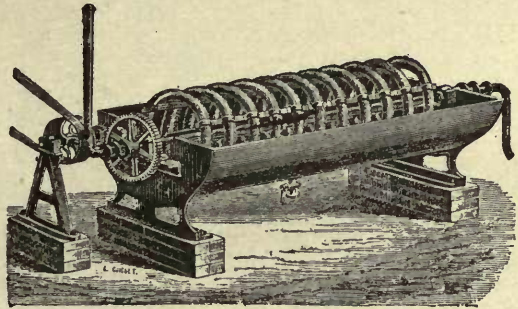

Fig. 174.

In some cases the glycerol thus obtained (or after dilution with water), while still boiling, is decolorised by adding animal charcoal and filtering through a filter-press. This glycerol always contains a small quantity of dissolved salts. To purify it, its temperature is raised to 110° to 120° by means of superheated steam, the acids or more volatile products being thus eliminated. It is then distilled with superheated steam at 170° to 180°, at which temperature all the pure glycerol passes over. This is rectified in one apparatus at 22° Bé. and in a second, under diminished pressure and with superheated steam, to 28° Bé., at which concentration almost all the salt separates. In general the coloration produced on distillation is less with a slightly alkaline, than with an acid, glycerol. The vacuum distillation is sometimes effected by a triple-effect apparatus (Pick type, *see* Vol. I., p. 567; *also* section on Sugar), with which it is easy to remove the salt, as it separates without interrupting the distillation.

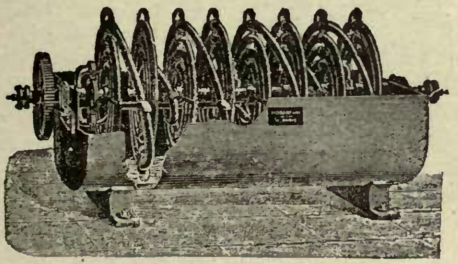

Fig. 175.

These forms of apparatus for purification and distillation are named after their inventors (Hagemann, Scott, Jobbins, van Ruymbeke, Lehmann, Heckmann, etc.).

The Heckmann process consists in distilling the aqueous glycerine, already concentrated to beyond 20° Bé., in a boiler, *A* (Fig. 176), into which steam superheated to 200° to 220° and under half an atmosphere pressure is passed by means of a perforated coil; the temperature of the liquid should not exceed 170°, since otherwise a small part of the glycerol decomposes. In order to prevent the scum being carried over with the steam and glycerol, a perforated disc, *a*, fitted with a vent-pipe is fixed two-thirds of the way up the boiler. The vapours issue by the pipe *B*, and are condensed in the reservoir, *C*, which is heated to 80° to 90° with indirect steam circulating in the jacketed bottom, *D*. Above the reservoir is a rectifying column, with a dephlegmator, *K*, similar to, but much lower than, that used for the rectification of alcohol (*see* p. 158).

During the distillation, a slight vacuum is maintained in the whole apparatus by means of a suction pump, *V*, so that principally water-vapour and only a little glycerol are evolved from the reservoir, *C*. The glycerol vapour separates in the column and returns to the reservoir, whilst the condenser, *M*, condenses only the water-vapour, which is controlled by its density, colour, and taste in the test-glass, *N*, and is then collected in the tank, *O*. In *C* the glycerol finally reaches a concentration of 95 to 99 per cent.

The rectifying column is sometimes replaced by a series of communicating, vertical copper tubes (Fig. 177) which fractionally condense the glycerol- and water-vapours from the boiler, *B* (heated partly by direct fire), into which passes steam from *v*, superheated in the furnace, *T*. By means of the pump, *Z*, a vacuum is maintained in the whole apparatus, so that, as the distillation proceeds, fresh glycerine from the reservoir, *A*, may be drawn into the boiler. In the first cylinder or condensing tube, which soon reaches a temperature of 100°, almost pure glycerol separates, whilst in the succeeding tubes, cooled only by the surrounding air, more and more dilute glycerine and finally water separate. Below each tube is a horizontal cylinder, these serving to collect the glycerols of different concentrations, some of which are subjected to redistillation. In this way is obtained the best *dynamite glycerine*, which must have a specific gravity of 1·263 (98 to 99 per cent.), and should not contain lime, sulphuric acid, chlorine, or arsenic. To eliminate traces of colour and empyreumatic products, the liquid is digested with boneblack (washed with acid and dried); the final portions of water are expelled by heating in a vacuum.

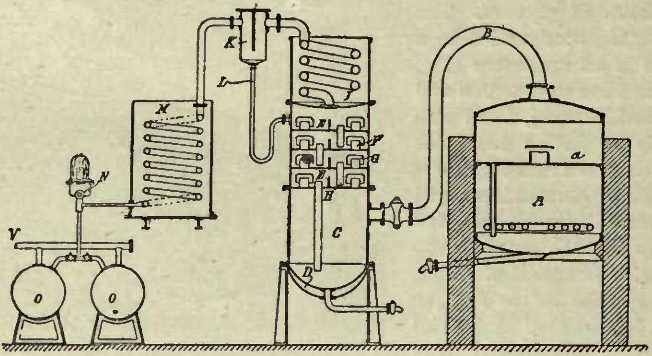

Fig. 176.

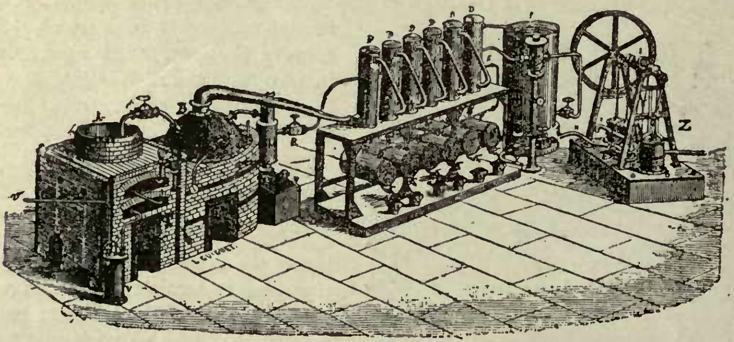

Fig. 177.

Besides by means of boneblack or special vegetable charcoal, complete decoloration may also be effected by sodium hydrosulphite or, better, by the zinc-formaldehyde sulphoxylate compound (*see* Vol. I., p. 588). Very pure glycerol has been obtained by maintaining it at 0° for some time and then inducing crystallisation by a few pure crystals obtained separately by cooling to — 40° (Kraut's process). The degree of purity is increased by a second crystallisation.

Purification by an osmotic process has also been attempted but with unsatisfactory results.

During the last few years the glycerine liquids from the biological or catalytic decomposition of fats (*see* section on Fats) have also been worked up: they are first neutralised or, better, rendered slightly alkaline with milk of lime and, after being left for some time, the liquid is decanted or filtered off, concentrated to 15° Bé. *in vacuo*, again allowed to stand to deposit a further quantity of lime, decolorised by passing through a carbon filter and again concentrated to 28° Bé.

Various attempts have also been made to recover the glycerine from the waste liquors from the manufacture of alcohol, but as yet without much success (Ger. Pats. 114,492, 125,788, 129,578, 141,703, and 147,558).

STATISTICS AND PRICES. The production and trade in glycerine (from stearine and soap-works) in different countries is shown by the following figures (tons): [1]

			1890	1900	1905	1908	1910	1912	1913	1918
France	prod.	stearine	6,000	—	—	12,000	—	14,000	—	—
		soap	3,500	—	—					
	exp.		3,856	7,450	—	7,000	—	6,811	—	—
Germany	prod.	stearine	3,000	2,000	—	—	—	3,000	—	—
		soap	2,000	8,000	—	—	—	9,000	—	—
	exp.		—	2,730	—	1,580	—	—	—	—
	imp.		—	—	—	5,373	—	—	—	—
Great Britain	prod.	stearine	1,200	—	—	16,000	—	—	—	—
		soap	5,500	—	—					
	exp.		—	—	—	10,000	12,000	—	—	—
	imp.		—	—	—	—	3,360	—	—	—
Italy	prod.		180	—	190	215	294	220	505	—
	exp.		—	—	—	833	1,763	2,282	1,259	—
	imp.		—	—	—	198	270	789	761	6,828
United States	prod.	stearine	—	—	10,000	—	—	20,000	—	—
		soap	—	—	13,000					—
	exp.		—	—	—	—	—	—	—	10,000
	imp.		—	—	—	16,000	18,000	—	—	—
Whole world	prod.	stearine	26,000	40,000	—	72,000	80,000	—	—	—
		soap	14,000	40,000	—					

The following qualities of glycerine are distinguished: [2] (A) *Crude glycerine* from the

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[1] In 1910 Spain produced 2500 tons of glycerine, 893 tons being exported.

The annual output in Italy prior to the war amounted to about 350 tons of glycerine for pharmaceutical purposes, 100 tons of dark glycerine residues for use on the railways, and about 150 tons of pure glycerine for dynamite, for which also glycerine was imported. During the war the Italian imports were: 1914, 335 tons (1094 exported); 1915, 791 (40 exported); 1916, 1590; 1917, 4189, and 1918, 6828 (almost all from the United States), valued at £2,600,000.

Three-fourths of the French output is due to Marseilles, where, before the war, a single refinery produced 2500 tons yearly; the exports were mainly to the United States.

German imports and exports were as follows (tons):

	Crude Glycerine		Pure Glycerine	
	Imports	Exports	Imports	Exports
1910	4685	1688	914	2596
1911	5143	2463	1241	2394
1912	5875	2316	1186	3736
1913	5374	2237	1107	3937

[2] **Tests for Glycerine**: the *crude*, pale at 28° Bé., contains 0·5 per cent. of ash and is not rendered turbid by HCl, and only faintly so by lead acetate; that separated from sulphuric acid saponifications, besides having a bad smell and taste, gives 3 to 5 per cent. of ash and 84 to 86 per cent. of glycerine, a turbidity (fatty acids) or precipitate being produced by HCl or lead acetate. The glycerine to be used for nitroglycerine and dynamite is subjected to the following tests: the *water* is calculated from the loss in weight of 20 grams heated for ten hours at 100° and for a few hours at a slightly higher temperature. Five grams, after being heated in a platinum dish at 180° until no further evolution of vapour takes place, is weighed, and should then undergo no further diminution in weight when again heated for a short time; it is then ashed in the usual way and the ash tested for metals and salts. *Glycerine for nitroglycerine* should have been distilled at least once, should not contain sugar or fatty acids, should have a neutral reaction and should contain no lead, calcium, or other metals or foreign metalloids; only traces of Cl, As, and Fe are allowed: the specific gravity should exceed 1·26 at 15°. The purest glycerine (puriss). does not contain more than 0·03 per cent. of ash and not more than 0·2 per cent. of extraneous organic substances which do not evaporate at 175°, and for dynamite these two should not exceed 0·25 per cent. Oxalic acid is detected by neutralising with ammonia, acidifying with acetic acid and precipitating with $CaCl_2$. The glycerine content is determined from the density

candle- or soap-works; the saponification glycerine from candle-making is the better (since fats of higher quality are used for candles) and, although it is darker, it is more easily decolorised than that from soap lye. (B) *Refined glycerine*, which is subdivided into: pale, white, for dynamite, and chemically pure.

The *price* of glycerine has undergone considerable fluctuation owing to various causes, often to collusion between speculators. Thus between 1867 and 1880, it varied between £12 and £42 per ton, while financial manœuvres raised the price to £88 in 1881, since when the glycerine of soap lyes has been largely utilised. In 1884 the price of dynamite glycerine fell to £24 per ton.

In 1908–1909 the price of No. II dark brown crude glycerine at 24° Bé. was £15 per ton and at 28° Bé. £18; for the light brown variety, £23, and for the pale at 28° Bé. £40. Yellow refined at 28° Bé. cost £46; white refined No. I, £48 at 28° Bé. and £45 at 30° Bé.; free from lime for soap, £50 at 28° Bé. and £54 at 30° Bé. Finally the purest double-distilled for nitroglycerine at 31° Bé. cost £60 per ton. At the beginning of 1910 these prices were increased by 25 per cent., and towards the end of 1910 by 50 per cent. or even 70 per cent. At the beginning of 1911 they were still higher, mainly owing to the large amount required in North America for making dynamite for the Panama Canal and other public works. During the European War glycerine for dynamite cost as much as £320 to £360 per ton.

C. TETRA- AND POLY-HYDRIC ALCOHOLS

These are usually sweet, crystalline substances which decompose near their boiling-points. They are distinguished one from another by the crystalline forms of their phenylhydrazine derivatives.

They do not reduce Fehling's solution, and hence differ from the carbohydrates, but are derived from these by reduction.

The *valency of an alcohol* is given by the number of alcoholic hydroxyls it contains, and hence by the number of monobasic acid residues it can fix to form a neutral ester. Acetic anhydride serves well for this purpose, the hydrogen atoms of the hydroxyl groups being replaced each by an acetyl group, $CH_3 \cdot CO$:[1]

$$\underset{\text{Mannitol}}{C_6H_8(OH)_6} + 6(CH_3 \cdot CO)_2O = 6CH_3 \cdot COOH + \underset{\text{Hexacetylmannitol}}{C_6H_8(O \cdot CO \cdot CH_3)_6}.$$

(the air-bubbles being removed by heating), use being made of the Table on p. 219; in Germany a special Berthelot scale is used indicating one degree higher than the Baumé scale, 26° Berthelot corresponding with a specific gravity of 1·210, 28° with 1·230, 29° with 1·240, and 30° with 1·250. The index of refraction is determined at the temperature indicated in the Table. In many cases the glycerine is estimated directly by means of the *acetyl number* (*see* succeeding Note), but the method in which the glycerine is oxidised by hot permanganate and potassium hydroxide to oxalic acid and the latter precipitated as calcium oxalate should be rejected. The fairly rapid Hehner-Richardson-Jaffe method, improved by Tortelli, is used more successfully: the glycerine is destroyed with dichromate and sulphuric acid, and the amount of dichromate used up (or, according to Gautter and Schulze, the amount of CO_2 evolved) measured by titration with sodium thiosulphate, or, better, ferrous ammonium sulphate. This method assumes that the glycerine contains no chloride, nitrate, or extraneous organic matter; these impurities may, in any case, be eliminated by means of silver oxide (chlorides), and lead acetate and calcium carbonate (organic matter), decoloration being then effected by heating with animal charcoal.

[1] In this way is determined the so-called *acetyl number* which is so widely used in the analysis of fats and oils. With these, the test is made on the insoluble *fatty acids* obtained by saponifying 40 to 50 grams of the fat with 40 c.c. of KOH solution (sp. gr. 1·4) and 40 c.c. of alcohol, this mixture being heated for half an hour on the water-bath, after which it is diluted with a litre of water and boiled for three-quarters of an hour in an open beaker to eliminate the alcohol. The liquid is acidified with sulphuric acid and boiled until the fatty acids separate in a transparent condition, when they are removed by means of a separating funnel, washed twice with hot water and dried in an oven at 100° to 105°. To determine the acetyl number, a few grams of the substance containing the hydroxyl groups (or about 20 grams of hydroxylic fatty acids) is treated with two or three times its volume of acetic anhydride and a few drops of concentrated sulphuric acid (formerly in place of the sulphuric acid fused sodium acetate, in quantity equal to the acetate anhydride, was used, the mixture being heated for two hours on the water-bath in a reflux apparatus). The mass heats spontaneously, and in a few minutes acetylation takes place; it is then allowed to cool, calcium carbonate being added to precipitate the sulphuric acid, and the liquid filtered. The filtrate is distilled or evaporated to separate the acetate in a liquid or crystalline condition.

In the case of the fatty acids, the filtrate is, however, diluted with 600 to 700 c.c. of water

Esters may also be prepared with bromobenzoic acid, the bromine in the resultant product being determined and the number of hydroxyl groups deduced therefrom. Well-defined compounds are also formed with benzaldehyde and are employed in separating the constituents of different mixtures.

ERYTHRITOL (Butantetrol), $OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$, is found in nature in the free state in *Protococcus vulgaris*, and as orsellinic ester (erythrin) in lichens and other algæ. It forms crystals, m.-pt. 112°, b.-pt. 330°, and is slightly soluble in alcohol and insoluble in ether. It is obtained by decomposing *d*-glucose or synthetically from crotonylene, and its constitution is deduced from the fact that it yields secondary normal butyl iodide on reduction with hydriodic acid. A similar reaction takes place with the higher polyvalent alcohols with normal chains. The four possible stereoisomerides are known, the most common being the one now described, which is optically inactive.

PENTA-ERYTHRITOL has the formula $C(CH_2 \cdot OH))_4$, and melts at 253°.

ARABITOL, $C_5H_7(OH)_5$ (Pentahydroxypentane), crystallises in acicular prisms, m.-pt. 102°, has a sweet taste and is formed by reducing the corresponding sugar, arabinose, with nascent hydrogen; reduction of xylose similarly yields xylitol.

MANNITOL, $C_6H_8(OH)_6$ (Hexanhexol), occurs abundantly in the vegetable kingdom (the larch, celery, sugar-cane, *Agaricus integer* containing 20 per cent. of mannitol, etc.), but especially in the manna ash (*Fraxinus ornus*), the dried juice of which forms ordinary *manna;* [1] from this alcohol extracts pure mannitol, which may be decolorised by repeated

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and boiled for thirty to forty minutes in an open beaker to remove the acetic acid, a slow current of CO_2 being passed into the bottom of the liquid to prevent bumping. The supernatant liquid is then siphoned from the acetyl compound, which is boiled with another 500 c.c. of water and so on, this operation being repeated until the washing water no longer has an acid reaction. The acetylated derivative is then collected on a filter, washed and dried in an oven.

Of this compound, 0·5 to 1 gram is dissolved in pure, neutral alcohol, and the solution heated for forty-five minutes on the water-bath in a 150 c.c. flask, fitted with a reflux condenser, with a definite volume (30 to 50 c.c.) of seminormal alcoholic potash. When cold, the liquid is titrated with seminormal hydrochloric acid in presence of phenolphthalein to determine the excess of alkali which has not taken part in the splitting of the acetic ester.

One hydroxyl group for every gram-mol of substance corresponds with 56 grams of KOH fixed. With the fatty acids, which contain also the carboxyl group, the procedure is as follows: 3 to 4 grams of the acetyl derivative is dissolved in pure, neutral alcohol and the acidity of the carboxyl group (*acetyl acid value*) determined by titration with N/2-alkali; the neutralised liquid is boiled with a known volume in excess of N/2-alcoholic potash for a short time on the water-bath, retitration with N/2-hydrochloric acid giving the excess of alkali not combined with acetyl groups. The alkali combined (after the first neutralisation), expressed in mgrms. of KOH per 1 gram of acetyl compound gives the *acetyl number.* With the fatty acids the sum of the acetylated acid number and the acetyl number is termed the *acetyl saponification value.* From the acetyl number (N), the molecular magnitude (M), of the alcoholic substance may be deduced by the formula: $M = \frac{56,100}{N} - 42$.

[1] Manna is extracted more particularly from *Fraxinus ornus* and *Fraxinus rotundifolia*, which are widespread in Sicily and Calabria and from which it readily flows through long vertical incisions made in summer and autumn. It seems to occur in the rising sap before this reaches the leaves, and is thought by some to be produced by enzyme actions. Crude, commercial manna contains 12 to 13 per cent. of water, 10 to 15 per cent. of sugar, 32 to 42 per cent. of mannitol, 40 to 41 per cent. of mucilaginous substances, organic acids and nitrogenous matter, 1 to 2 per cent. of insoluble substances and 1 to 2 per cent. of ash. *Australian manna* (from *Myoporum platycorpum*) contains as much as 90 per cent. of mannitol. In the neighbourhood of Palermo, *Fraxinus rostrata*, which gives an inferior manna, is cultivated.

The manna tree grows in fertile, dry and even rocky soil and is incised in its tenth year and in the following ten or fifteen years. It is then cut back and the new branches incised in the seventh year and the succeeding ten or fifteen years. It is then again cut back, this procedure being continued for eighty or a hundred years. One hectare with 4500 trees gives as much as 100 kilos of manna per annum. It is harvested in August and September.

Manna is used as a mild purgative for children. It has a sweetish taste, is soluble in water or alcohol, and, besides mannitol, contains various sugars such as *stachyose* and *mannatriose.*

To extract the mannitol, the crude manna is dissolved in half its weight of water containing white of egg. The solution is boiled for a few minutes and strained, and the filtered mass, solidified by cooling, pressed in bags, or, better, centrifuged and washed at the same time with a large quantity of cold water. It is redissolved in water and the solution boiled with animal charcoal, filtered under pressure, crystallised and centrifuged. The mother-liquors are used to dissolve fresh quantities of the crude manna. The fineness of the crystals depends on the concentration and on the temperature of the air; in some cases the crystallisation is disturbed by continually stirring the mass.

treatment with charcoal. In manna it was discovered by Proust in 1806. It is obtained synthetically by reducing fructose or glucose: $C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$.

The optically inactive, lævo- and dextro-rotatory forms are known, the last being the most common; the optical activity is slight, but is rendered more apparent by the addition of borax. When heated it loses water giving anhydrides (*mannitan*, $C_6H_{12}O_5$, and *mannide*, $C_6H_{10}O_4$); in a vacuum it distils unchanged.

One hundred parts of water dissolve 16 parts by weight of mannitol at 16°.

From alcohol it crystallises in triclinic acicular prisms and from water in large rhombic prisms having a sweet taste and melting at 160°.

Stereoisomeric with mannitol is **DULCITOL**, $C_6H_8(OH)_6$, which occurs in a number of plants and in Madagascar manna. It forms sweet, monoclinic prisms, m.-pt. 188°, and is almost insoluble in water, even in the hot. Synthetically it may be prepared by reducing lactose and galactose. It is optically inactive even in presence of borax.

Another stereoisomeride of mannitol is sorbitol, which melts at 104° to 109°, or at 75° when crystallised with $1H_2O$. It may be obtained synthetically by reducing *d*-glucose or *d*-fructose. In presence of borax it shows a slight dextro-rotation.

Other stereoisomerides are **TALITOL** and **IDITOL**; these isomerides are usually separated by means of the acetals they form with benzaldehyde.

DD. DERIVATIVES OF THE ALCOHOLS

A. DERIVATIVES OF MONOHYDRIC ALCOHOLS

I. ETHERS

These are generally formed by eliminating 1 mol. of water (for example, by concentrated sulphuric acid or by hot hydrochloric acid) from 2 mols. of alcohol, which condense to form 1 mol. of ether in the same way as 2 mols. of an acid give an anhydride:

$$\begin{array}{l} C_2H_5\cdot OH \\ CH_3\cdot OH \end{array} = H_2O + \begin{array}{l} C_2H_5 \\ CH_3 \end{array}\!\!>O.$$

Ethers are not formed by secondary or tertiary alcohols. The first term of the series, methyl ether, is gaseous, and the succeeding terms become liquid and then solid as the molecular weight increases, the ethereal odour of the first members being gradually lost.

The empirical formulæ of the ethers show them to be isomeric with the alcohols, but their constitution results from Williamson's synthesis, according

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Sometimes the manna solutions are first subjected to lactic fermentation, by which means considerable quantities of calcium lactate are obtained; the mannitol is then extracted from the residual liquors.

Mannitol is not fermented by beer-yeast, but with chalk and sour cheese it gives a considerable amount of alcohol, volatile acids, carbon dioxide, and hydrogen. When cautiously oxidised with nitric acid, it forms *d*-mannose and *d*-fructose, whilst with the *Sorbose bacterium* it gives only the latter sugar.

Mannitol has a slight lævo-rotation (— 15°) which is increased by alkali and changed in sign by borax. It dissolves in 6·5 parts of water at 18°, in 80 parts of 60 per cent. alcohol at 15°, or in 1400 parts of absolute alcohol; it is insoluble in ether.

Manna in casks costs 3*s.* to 5*s.* per kilo; assorted, 1*s.* 7*d.*; in lumps, 9½*d.* The average price of manna (from Cefalu) on the Genoa Exchange gradually rose from about 2*s.* 1*d.* in 1901 to about 4*s.* 7*d.* in 1910, when pure crystallised mannitol cost 7*s.* to 10*s.* per kilo. The best qualities of manna are those from Cefalu, Gerace, and Smauro; of inferior quality is the Capaci variety, which is produced also at Cinisi, Belmonte, Castellamare del Golfo, etc. The Sicilian production, which represents almost the entire production of the world, was about 360 tons in 1900, 700 in 1902, 510 in 1905, 690 in 1906, 455 in 1908, and less than 300 (owing to the bad season) in 1910. The output of mannitol in 1910 was 50 tons, but usually about 300 tons of manna are treated per annum for the production of mannitol—about 100 tons—one-third or one-fourth of which is consumed in Italy.

The exports of manna from Italy are as follows (tons):

	1908	1910	1912	1913	1914	1915	1916	1917	1918
Tons . .	178	312	377	350	267	231	278	245	206
Value, £ .	26,285	—	105,560	—	48,510	—	83,400	—	70,000

to which they are obtained by the action of a sodium alkoxide on the halogen derivative of an alcohol:

$$C_mH_{2m+1}ONa + IC_nH_{2n+1} = NaI + C_mH_{2m+1} \cdot O \cdot C_nH_{2n+1}$$

If in the sodium alkoxide the sodium were not united to the oxygen, but directly with carbon, this reaction would give an alcohol and not an ether; indeed, if sodium ethoxide were $NaCH_2 \cdot CH_2 \cdot OH$, it would, with methyl iodide, give propyl alcohol: $CH_3I + NaCH_2 \cdot CH_2 \cdot OH = NaI + CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$. In reality, however, methyl ethyl ether, and not propyl alcohol, is obtained, this proving the constitution of the metallic alkoxides and of the ethers, in which all the hydrogen atoms are equivalent.

The interaction of silver oxide with alkyl halides (*see* p. 17) also leads to the formation of ethers: $2C_2H_5I + Ag_2O = 2AgI + C_2H_5 \cdot O \cdot C_2H_5$.

If the alkyl radicles of an ether are similar, it is a *simple ether*, *e. g.*, ethyl ether, $C_2H_5 \cdot O \cdot C_2H_5$, whereas if the radicles are different, the result is a *mixed ether*, *e. g.*, methyl ethyl ether, $C_2H_5 \cdot O \cdot CH_3$.

Sabatier, Senderens, and Mailhe (1909–1910) obtained ethers of different types, some mixed and of the aromatic series, by passing the superheated vapours of alcohols (250° to 350°) over metallic oxides (titanium, thorium, tungsten, or, best of all, aluminium). The yield is quantitative, no ethylene hydrocarbons being formed, as is the case when sulphuric acid is used. The process is continuous and pseudo-catalytic, unstable aluminium alkoxide being formed as an intermediate product: $(C_2H_5O)_6Al_2 = Al_2O_3 + 3(C_2H_5)_2O$. In some cases this general method may be advantageously employed industrially.

When the ethers are prepared from the alkoxides in alcoholic solution there should not be an excess of water (more than 50 per cent.) present, otherwise the alkoxide decomposes into alcohol and alkali hydroxide and no ether is formed.

Also when sulphuric acid (or HCl) is used in the preparation, an equilibrium sets in between the reacting products—intermediate and final—this equilibrium being regulated by the mass law, so that a certain yield cannot be exceeded except by eliminating some of the new products formed (*e. g.*, by gradually distilling the ether; *see later*):

$$(a)\quad C_2H_5 \cdot OH + H_2SO_4 = \underset{\text{Ethylsulphuric acid}}{C_2H_5 \cdot SO_4H} + H_2O.$$

$$(b)\quad C_2H_5 \cdot SO_4H + C_2H_5 \cdot OH = H_2SO_4 + C_2H_5 \cdot O \cdot C_2H_5.$$

The sulphuric acid is regenerated and can transform fresh alcohol into ether; theoretically, then, the initial quantity of sulphuric acid should be sufficient to transform an infinite quantity of alcohol into ether, but in practice it is necessary to add a small quantity of the acid each time, as some of it is used up in the formation of sulphur dioxide, ethylene, and sulphonated products. Thus, in practice the process is not continuous in the strict sense of the term, since in the phase (*a*) water is formed, and this cannot all be eliminated by distillation, but after a time accumulates in such quantity as to establish an equilibrium between the formation of ether and the decomposition of ethylsulphuric acid, alcohol and sulphuric acid thus being regenerated.

The ethers are very stable and scarcely react in the cold with alkalis, dilute acids, sodium or phosphorus pentachloride. When superheated with water and a little mineral acid, ether is converted back into alcohol:

$$C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4 = C_2H_5 \cdot OH + C_2H_5 \cdot SO_4H,$$

and the same change occurs on saturating ether at 0° with gaseous hydrogen iodide:

$$(C_2H_5)_2O + HI = C_2H_5 \cdot OH + C_2H_5I,$$

the hydrogen iodide subsequently converting the alcohol also into ethyl iodide; when mixed ethers are taken, the iodine unites preferably with the radicle containing the lesser amount of carbon. PCl_5 also decomposes the ethers on heating:

$$(C_2H_5)_2O + PCl_5 = POCl_3 + 2C_2H_5Cl.$$

The halogens give substitution products just as they do with the hydrocarbons, but nitric acid gives oxidation products.

In the ethers are reproduced all the cases of isomerism presented by the alkyl groups from which they are derived, there being consequently numerous cases of *metamerism* (*see* p. 18), *e. g.*, methyl amyl ether, $CH_3 \cdot O \cdot C_5H_{11}$, is metameric with ethyl butyl ether, $C_2H_5 \cdot O \cdot C_4H_9$, and also with dipropyl ether, $C_3H_7 \cdot O \cdot C_3H_7$, all these having the empirical formula $C_6H_{14}O$.

METHYL ETHER, $CH_3 \cdot O \cdot CH_3$ (Methoxymethane), is a gas, but liquefies at -- 23°, and then has the sp. gr. 1·617; it resembles ethyl ether. One volume of water dissolves 37 vols. of the gas, and 1 vol. of sulphuric acid 600 vols. of it.

ETHYL ETHER, $C_4H_{10}O$ (Ethoxyethane), $C_2H_5 \cdot O \cdot C_2H_5$. This was prepared for the first time in the sixteenth century by Valerius Cordus from spirit of wine. It was formerly thought to contain sulphur, and was therefore given the name *sulphuric ether*, still in use. Its true composition was established by Saussure and by Gay-Lussac (1807 and 1815), and the constitution was enunciated by Laurent and Gerhardt and confirmed experimentally by Williamson. It was thought for a long time that the sulphuric acid employed in the manufacture of ether possessed the sole function of fixing and subtracting water from the alcohol. Since, however, it was found that water formed in the reaction always distilled with the ether, this hypothesis became invalid, and Berzelius and Mitscherlich attributed the reaction of etherification to the catalytic action of the sulphuric acid.

Later on Liebig maintained that the ether is formed by the direct decomposition of the intermediate product (ethylsulphuric acid) with separation, in the hot, of SO_3. Graham, however, succeeded in showing that ethylsulphuric acid, when heated alone at 140°, does not give ether, but that the latter is formed in presence of alcohol. In 1851 Williamson gave the true explanation of the process by dividing the reaction into two phases (*a* and *b*, *see* preceding page); the secondary products, explaining the loss of sulphuric acid (*see above*), were discovered later.

Etherification takes place also if the sulphuric acid is replaced by phosphoric, arsenic, boric, or hydrochloric acid.

Sulphur dioxide, which is formed and lost in this process, is not produced if the sulphuric acid is replaced by an aromatic sulphonic acid, for instance, $C_6H_5 \cdot SO_3H$, or the corresponding chloride, $C_6H_5 \cdot SO_2Cl$ (Kraft and Ross, Ger. Pat. 69,115), the temperature of the reaction being then slightly above 100°:

$$(a)\quad C_2H_5 \cdot OH + C_6H_5 \cdot SO_3H = H_2O + C_6H_5 \cdot SO_2 \cdot OC_2H_5.$$
$$(b)\quad C_2H_5 \cdot OH + C_6H_5 \cdot SO_2 \cdot OC_2H_5 = (C_2H_5)_2O + C_6H_5 \cdot SO_3H.$$

J. W. Harris's process (U.S. Pat. 711,656) may have an industrial future; in this, acetylene and hydrogen give ethylene which, with H_2SO_4, forms ethylsulphuric acid, the latter then forming ether under the action of water.

Good results are also given by the use of *methionic acid*, $CH_2(SO_3H)_2$, proposed by Schroeter and Sondag in 1908; with this acid all the higher ethers may be prepared and 10 per cent. of the acid (on the weight of alcohol) is sufficient to give a continuous distillation of ether.

Senderens transforms alcohol vapour quantitatively into ether by passing it over calcined, precipitated alumina heated exactly to 260° (*see* p. 227).

PROPERTIES. Ether is a colourless, very mobile liquid of pleasant odour, boiling at 34·9°, solidifying at − 129° if dry, and at −40° if aqueous, and melting at −113°; it has the sp. gr. 0·712 at 25°, 0·7196 at 15°, 0·7289 at 6·9°, or 0·736 at 0°. Contamination of ether by water and alcohol may be detected at once by the specific gravity, which reaches the value 0·735 at 15° when the maximum proportion of water, namely, 7·5 per cent., is present. Commercially the density of ether is given in degrees Baumé (scale for liquids lighter than water).

The vapour density of ether at various temperatures in millimetres of mercury is as follows:

Temperature	−20°	−10°	0°	+10°	20°	30°	40°	50°	70°	90°	110°	120°
Pressure .	67·5	113·4	183·4	286·4	433	636	910	1271	2308	3898	6208	7702

On evaporation, it produces intense cold. It inflames very readily, but is not inflammable when mixed with 35 to 50 per cent. of carbon tetrachloride. With air it forms explosive mixtures (p. 34). It is obtained anhydrous by distilling over a little sodium.

J. Meunier (1907) has found that mixtures of ether vapour and air are inflammable and explosive when they contain between 75 and 200 mgrms. of ether per litre of air.

As ether vapour is much heavier than air (mol. wt. 74), it tends to collect in a dense, invisible layer on the floor or bench and may cause fire or explosion. It is soluble in concentrated hydrochloric acid. In the pure, dry state it is stable in the air, but it assumes an acid reaction if water or alcohol is present.

Water dissolves 6·5 per cent. of ether at 19°, and ether dissolves about 2·25 per cent. of water at 20°. When 20 c.c. of water is shaken in a cylinder with 20 c.c. of pure ether and then left at rest, the volume of the aqueous layer increases by 2 c.c. (solubility of ether in water; a small portion of the water passes into the ether); if the ether contain alcohol, the increase in volume of the water will be greater than 2 c.c., whilst if much alcohol be present, a single solution will be formed. Addition of water to a solution of one part of ether in three parts of alcohol results in dissolution of the water and in separation of a little of the ether, whilst in a solution of one part of ether in four parts of alcohol water dissolves without causing separation of ether. Aqueous ether may be recognised by the turbidity produced on shaking it with a small quantity of carbon disulphide. Ether dissolves in large amount in sulphuric acid (monohydrate), forming ethylsulphuric and ethionic acids and ethyl sulphate; 92·5 per cent. sulphuric acid readily dissolves ether almost or quite unchanged, but when heated, this solution forms ethyl sulphate and ethionic acid, which at a high temperature yields ethylene (1 vol. of sulphuric acid dissolves 1·67 vols. of ether). If, however, the sulphuric acid is diluted to 55° Bé. (after fixation of the ether), the ether may be recovered more completely (*see* note, p. 232).

It is an excellent solvent for many organic substances, especially for fats. It combines with certain inorganic substances (chlorides of tin, aluminium, phosphorus, antimony, etc.) as ether of crystallisation. With chlorine in the cold it gives successively: *monochloroethyl ether*, $CH_3 \cdot CHCl \cdot O \cdot C_2H_5$ (b.-pt. 98°); *ethyl dichloroethyl ether*, $CH_2Cl \cdot CHCl \cdot O \cdot C_2H_5$ (b.-pt. 145°); *ethyl trichloroethyl ether*, $CHCl_2 \cdot CHCl \cdot O \cdot C_2H_5$ (b.-pt. 170° to 175°), and *pentachloroethyl ether*, $(C_2Cl_5)_2O$, which boils at 68°, decomposing into C_2Cl_6 and *trichloroacetyl chloride*, $CCl_3 \cdot CO \cdot Cl$. Ether dissolves Br, I, $FeCl_3$, $HgCl_2$, $AuCl_3$, and chromic acid.

The action of light on ether produces small quantities of hydrogen peroxide, acetaldehyde, acetic acid, and vinyl alcohol. In contact with platinum black it ignites. When poured into a cylinder of chlorine it explodes and forms hydrogen chloride, whilst in the dark the slow reaction yields perchloroether.

Ether is an *anæsthetic* and was used as such before chloroform; it is again coming into use at the present time, as it is less dangerous, although it produces certain disturbing effects, for example, in the lungs. For this purpose it must be used in a highly purified condition; use of a cork in the bottle is sufficient to alter it.

When mixed with liquid carbon dioxide, it lowers the temperature to 79·5° below zero. It decomposes at above 500°, giving acetaldehyde.

INDUSTRIAL PREPARATION OF ETHER. Use was formerly made in many works of Süssenguth vessels, which are double-walled and made of iron and lead-lined. Later large iron pots, homogeneously leaded, were adopted, these being heated by high-pressure steam circulating either through a jacket or false bottom, or, more efficiently, through leaded copper coils arranged inside the vessel (*e. g.*, Barbet type, Fig. 178). At 135° to 140°, however, these wear out within a few months, even when made of heavy lead castings. Hempel endeavoured to lessen this trouble by making the lower half of the vessel of a single casting of hard lead, with the heating coils in the thickness of the walls; such vessels, although very expensive, are highly durable and require less frequent repair.

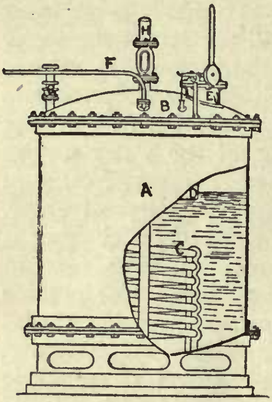

FIG. 178.

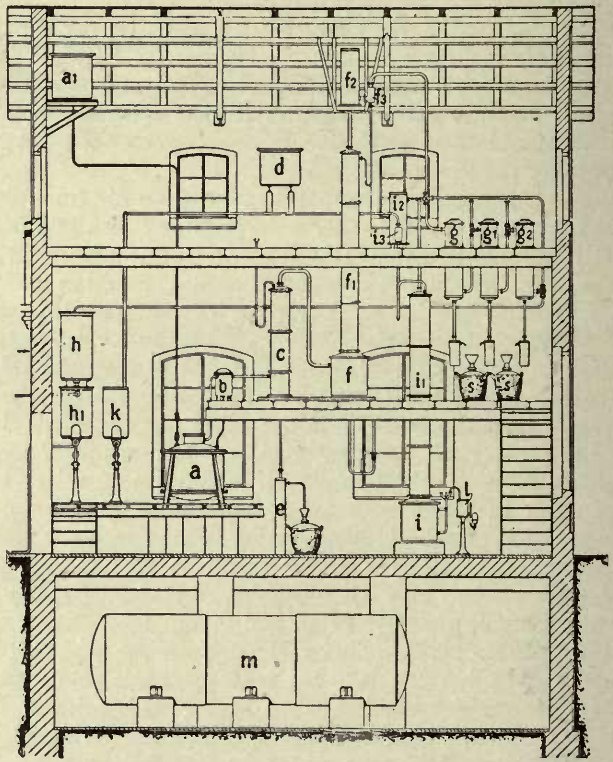

FIG. 179.

Until a few years ago crude ether, contaminated with water, alcohol and sulphur dioxide was made and then subjected to purification and rectification in another part of the works. Nowadays, however, general use is made of continuous process plants, which give directly pure ether, these being constructed by Messrs. Barbet (France), Eckelt (Berlin), and F. H. Meyer (Hanover). Fig. 179 shows the arrangement of an ether plant designed by H. Meyer: The pot *a* contains the mixture of alcohol (5 parts of 90 per cent., free from fusel oil) and sulphuric acid of 66° Bé. (9 parts, free from nitric and nitrosylsulphuric acids when copper vessels are used), this being heated by means of indirect steam to the temperature at which ether forms. From the tank *a′*, situated just under the roof, a continuous, regular stream of alcohol flows into *a*, and is there converted into crude ether, the vapour of which, after traversing the safety vessel *b*, where spray is retained, is washed with soda solution in the column *c* and then rectified in the column *f*. Here mainly the water and alcohol are condensed, the aqueous alcohol descending to the rectifying column

ii_1, where the water is discharged at the bottom, while the alcohol vapour passes to the dephlegmator i_3 and then to the condenser k; the pure concentrated alcohol is collected in the tank m. The rectified ether vapour from the column ff_1 proceeds to the dephlegmator f_2f_3, and the liquid ether through the three purifying and drying cylinders g, g_1, and g_2 to the carboys *ss*. The ether vapour escaping from g, g_1, and g_2 is condensed in the coil h by means of brine from a refrigerating plant and the condensate collected in h_1.

Some manufacturers use a mixture of 5 parts of 95 per cent. alcohol and 12 parts of sulphuric acid of 66° Bé.

Theoretically 124·3 parts of pure alcohol are required per 100 parts of ether. The *practical yield* of ether is about 95 per cent. of the theoretical, about 0·5 kilo of sulphuric acid being consumed per 100 kilos of ether.

Heckmann's apparatus for working on a small scale is shown in Fig. 180: A is the alcohol reservoir which feeds the alcohol regularly through the tap, a, and the glass vessel, b, to the still, B, containing the sulphuric acid; indirect steam under pressure is supplied to the coil, e. The ether continually distilling over is condensed in the coil, C, immersed in cold water.

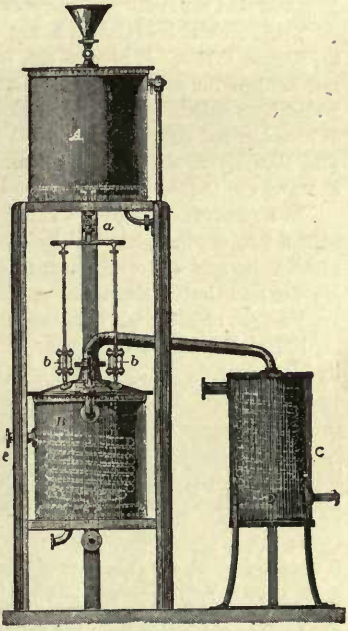

FIG. 180.

The premises where the distilling apparatus is situated are usually separated by thick walls from the condenser, in order to avoid the danger of fire and explosion. Some premises are fitted with channels and draught-apparatus for rapidly dispersing any vapour which may find its way into the air. The distilled vapour is condensed in closed apparatus, the only outlet to which is a tube opening on the roof. The maximum detonation occurs when 1000 litres of air contains 125 grams of ether vapour, but slight detonations also take place with 38 grams or 200 grams of the vapour; in the last case the gaseous mass is inflamed by a lighted substance or an electric spark.

If the temperature of etherification exceeds 140°, the yield diminishes, as a considerable quantity of ethylene is then formed: $C_2H_5 \cdot OH = H_2O + C_2H_4$. On the other hand, if the temperature falls below 130°, a large amount of alcohol distils without reacting.

The alcohol for making ether is denatured so as to be exempt from taxation, and in Germany animal oil (Dippel's) is added, this being then fixed and decomposed by the sulphuric acid. In Italy the alcohol is denatured with sulphuric acid.

D. Annaratone (Ger. Pat. 231,395, 1909) obtains increased yields of ether by passing alcohol vapour, superheated to 130°, into a column filled with pebbles, among which the sulphuric acid is circulated or sprayed; for 100 kilos of ether only 180 kilos of steam is required for heating instead of 700 kilos used in the old process. From the top of this column issue the ether vapour and the excess of alcohol vapour, the latter being condensed in a superposed rectifying column kept at a convenient temperature; the ether vapour is rectified in a subsequent column, where a little alcohol is condensed, and then passes to the refrigerating coils, in which it is completely condensed. The condensed alcohol is brought continuously to the desired concentration by means of a suitable rectifying column.

P. Fritzsche (1912) suggests the manufacture of ether by fixing the ethylene of oil-gas (*see* p. 64) by means of sulphuric acid, the resulting ethylsulphuric acid being diluted and heated to give ether and sulphuric acid.

USES AND PRODUCTION. Ether is used in small quantity as an anæsthetic, and in large quantities in the manufacture of collodion and artificial silk (1000 kilos of silk require about 5000 kilos of ether), as well as for smokeless powders (Powder B).[1] It serves also

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[1] **Recovery of ether from the air.** In the manufacture of smokeless powders and especially of powder B (*see later:* Explosives), enormous quantities of ether, mixed with alcohol, are used. In the Ferrania (Savona) works of the Società Italiana Prodotti Esplodenti, where powder B

as a solvent for numerous organic compounds in dye and perfume factories. In Ireland it is drunk as a liqueur—a refined form of alcoholism.

The amount of ether manufactured in Germany in 1902 was about 2000 tons, without counting that now made in large quantities for the production of artificial silk by the Chardonnet-Lehner process.

In Italy large amounts of ether were manufactured prior to 1910 when the artificial silk works used the Chardonnet process. During the European War it was made for preparing smokeless powder (Powder B); it is protected by a Customs duty of £72 per ton. In 1907, Gulinelli's distillery (Ferrara) alone produced 359 tons of ether. Owing to the crisis in the Italian artificial silk industry, the production had fallen considerably in 1910.

Ether exempt from duty was sold in Germany before the war at £40 per ton if its sp. gr. was 0·722, whilst the price of the pharmacopœial product, sp. gr. 0·720, was £90. Taxed ether, distilled over sodium and chemically pure, cost 4*s.* per kilo. In 1909, ether for artificial silk manufacture cost £2 11*s.* per hectolitre in Belgium and £2 14*s.* in Austria. In general ether costs one and a half times as much as alcohol.

TESTS FOR ETHER. Ether containing water or alcohol has a specific gravity between 0·720 and 0·733. When 20 c.c. of ether is shaken with 5 c.c. of water, the latter should not assume an acid reaction. Ozone or hydrogen peroxide may be detected by means of potassium iodide solution, which is turned brown in the dark in the course of an hour. White ignited copper sulphate is rendered green or blue by aqueous ether. Eder (1876) and Dan Tyrer showed that cadmium iodide is insoluble in absolutely dry ether, 0·64 per cent. of the iodide being dissolved for each 0·1 per cent. of water present.

In a mixture of alcohol and ether, Fleischer and Frank (1907) determine the proportions of the two components by shaking 10 c.c. of the mixture in a graduated tube with 5 c.c. of benzene and 6 c.c. of water: the increase in volume of the water shows the amount of alcohol and that of the benzene the amount of ether.

Various chlorinated derivatives of ether are known.

Ethyl Peroxide, $C_2H_5 \cdot O \cdot O \cdot C_2H_5$, is prepared by introducing ethyl groups into hydrogen peroxide by means of ethyl sulphate; it is a liquid, b.-pt. 65°, difficultly soluble in water and very readily inflammable, but is moderately stable towards chemical reagents.

In 1901 Baeyer prepared also the **Hydrate of Ethyl Peroxide, $C_5H_2O \cdot OH$,** as a colourless liquid, which possesses strong oxidising properties, dissolves in water, boils at 95°, and forms barium and other salts.

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is made, a plant capable of producing 20,000 kilos of ether per day is at work. In some of the large French works making powder B, the daily consumption of ether exceeds 100 tons, although 50 per cent. of it is recovered. The recovery of the ether is hence a problem of great importance. The air drawn from the galleries or chambers where the powder B (which contains about 35 per cent. of ether and 18 per cent. of alcohol) is dried contains as much as 400 grams of ether and alcohol per cubic metre. Part of this air is passed through a refrigerating chamber at − 15° and issues with only 20 to 30 grams of ether per cubic metre; it is then mixed with the portion which has not been cooled and again traverses the drying galleries or chambers at 40°, and thus becomes saturated again with alcohol and ether. This air is circulated by means of fans having a capacity of 10,000 to 15,000 cu. metres per hour; the part which is cooled constitutes only one-sixth or one-tenth of the whole volume. The solvent condensed by the cooling contains 60 per cent. of ether and 40 per cent. of alcohol. After this treatment the powder B still contains more than 20 per cent. of solvent and is dried completely in a gentle current of air, which takes up less than 35 grams of ether-alcohol per cubic metre and is usually not passed through the recovery apparatus. By this system about 56 per cent. of the ether and 36 per cent. of the alcohol used are recovered.

According to another system the ether is fixed by passing the air through concentrated sulphuric acid, which is afterwards diluted and heated, the bulk of the ether being thus liberated (*see* p. 229); about 60 per cent. of the total solvent is thus recovered. The use of castor-oil in place of sulphuric acid has also been suggested, this fixing both ether and alcohol and subsequently giving them up in good yield.

J. H. Bregeat fixes the alcohol and ether of the air by means of cresol (*see later:* Benzene derivatives), b.-pt. 195° to 205°, which absorbs even 5 grams of these compounds per cubic metre of air; all the alcohol and ether is recovered from the solution by heating the latter in iron vessels at 125° to 130°, the cresol being afterwards cooled and used again. In this way 92 to 95 per cent. of the alcohol and ether is recoverable, the cost being one-half of that incurred when sulphuric acid is used and one-third of that of the freezing method.

II. THIO-ALCOHOLS AND THIO-ETHERS

These have the same constitution as the alcohols and ethers, excepting that the oxygen is replaced by sulphur. They are very volatile and inflammable liquids, almost insoluble in water and having repulsive garlic-like odours; in the higher members, however, the odour diminishes and the solubility in water vanishes, although they continue to be soluble in alcohol or ether.

(*a*) **THIO-ALCOHOLS** (or **Mercaptans** or **Thiols** or **Alkyl Hydrosulphides**), $C_nH_{2n+1}SH$, have lower boiling-points than the corresponding alcohols. They are feebly acid in character and form salts called **Mercaptides**, *e. g.*, with mercuric oxide. They are soluble in concentrated alkali solutions. They may be regarded as hydrogen sulphide in which one atom of hydrogen is replaced by an alkyl radicle, *e. g.*, ethanthiol or ordinary **Mercaptan**, C_2H_5SH. As acids they are monobasic, and salts are formed with metallic sodium or potassium; the lead salts are yellow and are obtained by the action of lead acetate in alcoholic solution. Nitric acid transforms the mercaptans into *alkylsulphonic acids:* $C_2H_5SH + 3O = C_2H_5 \cdot SO_3H$.

With iodine, the salts of sodium, etc., give *disulphides:*

$$2C_2H_5SNa + I_2 = 2NaI + (C_2H_5)_2S_2,$$

which, with hydrogen, give mercaptans, and with nitric acid *disulphoxides*, $(C_2H_5)_2S_2O_2$; concentrated sulphuric acid gives disulphides and is itself reduced to sulphur dioxide.

(*b*) **THIO-ETHERS** (or **Alkyl Sulphides**), $(C_nH_{2n+1})_2S$, are neutral, readily volatile liquids, and afford a good illustration of the variability of the valency of sulphur (di- to hexa-valent).

They may be regarded as derived from hydrogen sulphide by replacement of the two hydrogen atoms by alkyl groups. With salts they form double *compounds*, *e. g.*, ethyl sulphide with mercuric chloride gives $(C_2H_5)_2S, HgCl_2$. They combine with halogens, giving, for instance, $(C_2H_5)_2SBr_2$, whilst when treated with dilute nitric acid they fix an atom of oxygen, yielding, *e. g.*, $(C_2H_5)_2SO$, *ethyl sulphoxide:* with more energetic oxidising agents, a further oxygen atom is taken up with formation of *sulphones*, *e. g.*, **Diethylsulphone**, $(C_2H_5)_2SO_2$. With hydrogen, the sulphoxides give sulphides, but the sulphides are not reduced. They combine with alkyl haloids, forming *sulphonium* compounds, *e. g.*, ethyl iodide and ethyl sulphide give **Triethylsulphonium Iodide**, $(C_2H_5)_3SI$, which reacts like metallic iodides with silver hydroxide, yielding **Triethylsulphonium Hydroxide**, $(C_2H_5)_3S \cdot OH$.

METHODS OF FORMATION. They are obtained: (1) by heating alkyl haloids or salts of alkylsulphuric acids with an alcoholic or aqueous solution of potassium sulphide or hydrosulphide: $C_2H_5Br + KSH = KBr + C_2H_5SH$; $2C_2H_5Br + K_2S = 2KBr + (C_2H_5)_2S$; $2C_2H_5 \cdot SO_4K + K_2S = 2K_2SO_4 + (C_2H_5)_2S$.

(2) By the action of phosphorus pentasulphide, P_2S_5, on ethers. *Mixed sulphides* also may be obtained by these and various other methods.

METHYL HYDROSULPHIDE (**Methanthiol**), $CH_3 \cdot SH$, is found among the gases from the anaerobic decomposition of proteins (for instance, in the intestines of animals). It is a nauseous liquid, lighter than water and boiling at 6°.

METHYL SULPHIDE, $(CH_3)_2S$, is a liquid, b.-pt. 37°, having a disagreeable ethereal odour.

ETHYL HYDROSULPHIDE (**Ethanthiol**, **Ethylmercaptan**, or **Mercaptan**), $C_2H_5 \cdot SH$, is a liquid, b.-pt. 36°, having a repulsive odour and is used for the preparation of *sulphonal.*[1] With sodium ethoxide in alcoholic solution it gives **Sodium Mercaptide**, C_2H_5SNa, in white crystals; **Mercuric Mercaptide**, $(C_2H_5S)_2Hg$, has also been obtained.

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[1] SULPHONAL is an important anæsthetic (*see* p. 118) and is obtained by saturating an acetone solution of ethylmercaptan with gaseous hydrogen chloride or by treatment with zinc chloride, the mercaptol, $C(CH_3)_2\ (SC_2H_5)_2$, thus formed being oxidised by potassium permanganate to form sulphonal, $C(CH_3)_2\ (SO_2C_2H_5)_2$, which crystallises in colourless, odourless, insipid

ETHYL SULPHIDE, $(C_2H_5)_2S$, is a liquid, b.-pt. 92°, insoluble in water, and forms a crystalline bromide, $(C_2H_5)_2SBr_2$.

ETHYL DISULPHIDE (Ethanodithioethane), $(C_2H_5)_2S_2$, boils at 151°, and is obtained by the action of iodine on mercaptan.

ETHYL SULPHOXIDE (Ethanosulphoxyethane), $(C_2H_5)_2SO$, is a dense liquid, soluble in water, and readily reducible.

ETHYLSULPHONE (Ethanosulphonethane, Diethylsulphone), $(C_2H_5)_2SO_2$, boils unchanged and does not undergo reduction.

TRIMETHYLSULPHONIUM IODIDE, $(CH_3)_3SI$, obtained from sulphur and methyl iodide, forms white crystals soluble in water and with silver hydroxide gives the **Hydroxide**, $(CH_3)_3SOH$, which is an energetic base and displaces ammonia from its salts.

III. ETHERS OF ALCOHOLS WITH INORGANIC ACIDS

Ethers formed from an alcohol residue and an acid residue are termed **Compound Ethers** or **Esters**. We shall here describe those derived from mineral acids and shall consider organic acid esters more in detail when the acids themselves have been studied. The esters may be regarded as derived either from acid by the replacement of the acid hydrogen by an alkyl residue, as with the salts, or from alcohols by replacement of the hydroxylic hydrogen by an acid radicle:

$$HNO_3 \quad . \quad . \quad . \quad KNO_3 \quad . \quad . \quad . \quad C_2H_5 \cdot NO_3$$

$$\text{or} \quad C_2H_5 \cdot OH \quad . \quad . \quad . \quad C_2H_5 \cdot O(NO_2) \quad . \quad . \quad . \quad C_2H_5 \cdot O(SO_3H).$$

Monobasic acids form only one class of esters, viz., *normal esters*.

Dibasic acids form two series of esters, *normal* and *acid*: *e. g.*, $C_2H_5HSO_4$, acid ester, and $(C_2H_5)_2SO_4$, normal ester.

Tribasic acids give three kinds of esters with constitutions analogous to those of the salts.

The **Normal Esters** are neutral liquids of agreeable odour, moderately volatile and insoluble in water.

The **Acid Esters** have acid reactions, are less stable, odourless, soluble in water, and volatile without decomposition.

In general, these esters are decomposed by alkali or water at a high temperature (150° to 180°), the components being regenerated; this change is known as *Saponification*: $C_2H_5NO_3 + KOH = C_2H_5 \cdot OH + KNO_3$.

FORMATION. (1) They are usually formed by the interaction of the components (absolute alcohol + acid), the water which gradually forms being fixed and the resulting ester distilled. With some acids, the corresponding salts in presence of concentrated sulphuric acid at 100° to 130° are taken, so that the acid is obtained in the nascent state and the ester driven off as it is formed. They are more readily obtainable by saturating the mixture of alcohol and salt with gaseous hydrogen chloride.

(2) From the silver salt of the acid and an alkyl iodide:

$$Ag_2SO_4 + 2C_2H_5I = 2AgI + SO_4(C_2H_5)_2.$$

(3) From the alcohol or alkoxide with the chloride of the acid:

$$SOCl_2 + 2C_2H_5OH = 2HCl + SO(OC_2H_5)_2; \quad \text{and}$$
$$POCl_3 + 3C_2H_5ONa = 3NaCl + PO(OC_2H_5)_3 \ (\textit{ethyl phosphate}).$$

(4) By passing the vapours of the acid and alcohol together over a catalyst as much as 50 per cent. of the ester is obtained.

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prisms, m.-pt. 125° to 126°, boiling unchanged at 300°. It dissolves slightly in water, alcohol or ether in the cold, but is readily soluble in boiling water or alcohol. When heated in a tube with powdered wood charcoal, it emits the repulsive odour of mercaptan, one-four hundred millionth of a milligram of which is detectable. It is sold at 24*s*. per kilo.

1. **ESTERS OF SULPHURIC ACID AND ALKYLSULPHURIC ACIDS.** These are generally prepared from fuming sulphuric acid and alcohol, or from silver sulphate and alkyl iodide or from alcohol and sulphuryl chloride,

$$SO_2Cl_2 + 2C_2H_5OH = 2HCl + SO_2(C_2H_5O)_2;$$

acid esters (*alkylsulphuric acids*) also exist. Tertiary alcohols do not form these esters.

Ethyl Sulphate, $(C_2H_5)_2SO_4$, is an oily liquid with an odour of mint and a pronounced acid character; it boils at 208° and is easily saponified, even by boiling with water alone. It is formed by heating ethylsulphuric acid:

$$2C_2H_5SO_4H = SO_4H_2 + SO_4(C_2H_5)_2.$$

Ethylsulphuric Acid, $C_2H_5SO_4H = (C_2H_5O \cdot SO_3H)$, is formed as an initial product in the manufacture of ether (p. 228). It is soluble in water and is distinguished from sulphuric acid by the solubility of its calcium, strontium, barium, and lead salts. It gives well crystallised salts, the potassium salt being largely used for preparing ethyl derivatives, *e. g.*, when it is dry-distilled with potassium bromide:

$$KBr + C_2H_5SO_4K = SO_4K_2 + C_2H_5Br.$$

2. **DERIVATIVES OF SULPHUROUS ACID: (a) Sulphurous Esters; (b) Sulphonic Acids.**

(*a*) **Ethyl Sulphite,** $SO_3(C_2H_5)_2$, and ethylsulphurous acid, $C_2H_5SO_3H$. The latter is known also in the form of salts and both are readily saponified, since the sulphur is not directly united with carbon: $CH_3 \cdot CH_2 \cdot O \cdot SO_2H$.

(*b*) **Ethylsulphonic Acid,** $C_2H_5 \cdot SO_3H$, is obtained by the reaction

$$C_2H_5I + SO_3Na_2 = NaI + C_2H_5SO_3Na;$$

or by oxidising the thioalcohols: $C_2H_5SH + O_3 = C_2H_5 \cdot SO_3H$; or thus:

$$2C_2H_5I + Ag_2SO_3 = 2AgI + (C_2H_5)_2SO_3 \text{ (\textit{ethyl ethylsulphonate})}.$$

Sulphonic acid compounds are not saponifiable; diethylsulphonic acid is saponifiable to the extent of one-half, since in the sulphonic acids the sulphur is united with carbon: $CH_3 \cdot CH_2 \cdot SO_2 \cdot OH$; the presence of hydroxyl is shown by the fact that with PCl_5 it forms $C_2H_5 \cdot SO_2Cl$, which with hydrogen gives *ethylsulphinic acid,* $C_2H_5SHO_2$, the salts of the latter reacting with alkyl haloids to form *sulphones.* Sulphonic acids are strong acids and give salts soluble in water.

3. **ESTERS OF NITRIC ACID.** These are explosive if heated rapidly and undergo saponification when boiled with an alkali. Tin and hydrochloric acid *reduce them,* giving **Hydroxylamine,** NH_2OH, the nitrogen being separated from the radicle as in saponification.

METHYL NITRATE, $CH_3O{\cdot}NO_2$, obtained by treating a mixture of methyl alcohol and potassium nitrate with concentrated sulphuric acid, is a colourless oil of unpleasant odour and sweet taste. It boils at 66°, has the sp. gr. 1·182 at 22°, is soluble in alcohol or ether, but insoluble in water, and is explosive and dangerous to handle.

Ethyl Nitrate: $C_2H_5O \cdot NO_2$, a liquid boiling at 86°, is obtained from absolute alcohol and concentrated nitric acid, the formation of the dangerous nitrous products being prevented by addition of a little urea.

4. **ESTERS OF NITROUS ACID.** These are easily obtained by passing nitrogen trioxide (N_2O_3) into the alcohols, or by treating the latter with alkali nitrites and sulphuric acid. They are reduced by nascent hydrogen, giving alcohol and ammonia.

Ethyl Nitrite, $C_2H_5O \cdot NO$, was at one time called *nitric ether.* Dissolved in alcohol, it bears the name *Spiritus ætheris nitrosi,* and is used to modify the taste of various substances. It is also used for preparing diazo-compounds.

5. **NITRO-DERIVATIVES OF THE HYDROCARBONS.** These are *isomeric with nitrous esters,* but they boil at higher temperatures than the latter and are distinguished from them by being non-saponifiable and by giving organic amino-compounds on reduction, as long as the nitrogen is not severed from the organic radical:

$$CH_3 \cdot NO_2 \text{ (nitromethane)} + 3H_2 = 2H_2O + CH_3 \cdot NH_2.$$

They are formed by treating alkyl iodides with silver nitrite:

$$CH_3I + AgNO_2 = AgI + CH_3 \cdot NO_2;$$

with the higher members of the series, the nitrous esters are formed at the same time and may be separated by distillation. Of the various methods of formation, mention may be made of that based on the action of *dilute* nitric acid, in the hot and under pressure, on the paraffins:

$$\underset{\text{Hexane}}{C_6H_{14}} + HNO_3 = \underset{\text{Nitrohexane}}{C_6H_{13} \cdot NO_2} + H_2O.$$

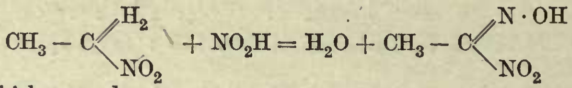
Concentrated nitric acid does not give nitro-compounds with the paraffins, but with aromatic hydrocarbons it reacts readily.

The difference in *constitution* between *nitro-derivatives, e. g.*, $H_3C \cdot NO_2$, and nitrous esters, *e. g.*, $H_3C \cdot O \cdot N : O$, explains their different relations as regards saponification.

This also confirms the hypothetical constitution of nitrous acid, $O : N \cdot OH$. The hydrogen of the carbon atom united to nitrogen may be partially substituted by metals or bromine, since it has acquired acid characters—for instance, $NaCH_2 \cdot NO_2$—but the acidifying influence of the nitro-group is not extended to the hydrogens of the other carbon atoms.

These nitroparaffins react with nitrous acid differently according as they are primary, secondary, or tertiary:

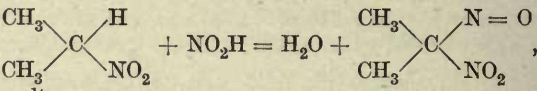
(*a*) Nitroethane,



$$CH_3-C\begin{matrix}\diagup H_2\\ \diagdown NO_2\end{matrix} + NO_2H = H_2O + CH_3-C\begin{matrix}\diagup N\cdot OH\\ \diagdown NO_2\end{matrix}$$

i. e., ethylnitric acid, salts of which are red.

(*b*) Secondary Nitropropane,



$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}C\begin{matrix}\diagup H\\ \diagdown NO_2\end{matrix} + NO_2H = H_2O + \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}C\begin{matrix}\diagup N=O\\ \diagdown NO_2\end{matrix},$$

propylpseudonitrole, which forms *blue* salts.

(*c*) Tertiary derivatives give no reaction.

These reactions serve well to distinguish *primary, secondary,* and *tertiary alcohols.*

Nitroethane may be used in the manufacture of explosives to lower the freezing-point of nitroglycerine.

CHLOROPICRIN, $CCl_3 . NO_2$, sp. gr. 1·692, boils at 112°, and is formed by the simultaneous action of nitric acid and chlorine on various organic compounds.

It is also obtained when a mixture of 60 grams of picric acid, 7 kilos of water and 1·5 kilo of calcium hypochlorite is heated by direct steam, the oily chloropicrin which distils over being washed with very dilute soda solution, decanted, dried, and distilled. It is soluble in alcohol, ether, or benzene and slightly so in water. It is a powerful and irritating lachrymatory and was largely used during the European War.[1] When superheated it

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[1] **CHEMISTRY AND THE WAR.** Among the poisonous gases and liquids used during the war are the following: phosgene, chlorine, bromine, cyanogen bromide, bromoacetone, aromatic arsines, nitrous vapours, acroleïn, allyl isothiocyanate, phosphorus, tin and arsenic chlorides, benzyl bromide, etc. The terrible *mustard gas* or *yprite* consists of *ββ'-dichloroethyl sulphide*, $S(CH_2 \cdot CH_2Cl)_2$, which is a yellowish, neutral, odourless oil of sp. gr. 1·27, m.-pt. 7°, b.-pt. 217° to 219° (decomposing slightly). It is almost insoluble in water, has a high vapour pressure, and produces extraordinarily lachrymatory and poisonous effects, even when brought into contact with the skin; it easily penetrates clothing. It was first used by the Germans against the British at Ypres on July 20, 1917, and afterwards at Nieuport and Armentières; on these two cities as many as 50,000 mustard gas shells per day were dropped for several days. In Germany 50 to 60 tons were made per day, in France 20 tons, and in America 40 tons. It is slowly saponified by hot alkali, and dissolves in alcohol, ether, benzine, etc.; with halogens it yields substitution products. By oxidising agents (hydrogen peroxide, permanganate, ozone, calcium hypochlorite, etc.) it is easily transformed into harmless compounds, $SO(CH_2 \cdot CH_2Cl)_2$ and $SO_2(CH_2 \cdot CH_2Cl)_2$.

In Germany mustard gas was made by heating glycol chlorohydrin on a water-bath with concentrated aqueous potassium sulphide and then evaporating and taking up the residue in absolute alcohol to get rid of sodium chloride. The syrupy residue left after expulsion of the alcohol was treated with phosphorus pentachloride, the mass being afterwards poured on to ice and the oil separated. In England (and America) mustard gas was made by the interaction of ethylene and sulphur chloride: $2C_2H_4 + SCl_2 = S(CH_2 \cdot CH_2Cl)_2$. The ethylene was obtained in 85 per cent. purity by passing alcohol vapour over lumps of kaolin heated at 500° to 600° in retorts, titanium oxide being used as catalyst; in England increased yields were obtained by using coke impregnated with phosphoric acid in place of kaolin and titanium. The reaction between C_2H_4 and SCl_2 (or S_2Cl_2) takes place at 30° to 35° and is regulated by cooling. To render the mustard gas more injurious and more volatile, it was mixed with carbon tetrachloride or chlorobenzene. Partial protection was afforded by rubber clothing and by bathing with permanganate.

Two mustard gas works were under construction in Italy when the Armistice was proclaimed.

explodes. When its solution or aqueous emulsion is reduced with iron turnings and a little acetic acid (other acids are unsuitable), it is transformed into *methylamine*. With stannous chloride it gives cyanogen chloride, while when heated at 100° with aqueous ammonia it yields *guanidine*.

NITROMETHANE, $CH_3 \cdot NO_2$, is obtained from methyl iodide and silver nitrate or, better (but still in poor yield) by distilling an aqueous solution of potassium chloroacetate (1 part) and potassium nitrite (3 parts), the distillate being separated from the water, dried with lime and rectified.

It forms an oil of ethereal odour and is denser than water, in which it is slightly soluble; it boils at 101° and burns with a pale flame. When reduced with iron and acetic acid it gives methylamine, while with HCl at 150° it yields hydroxylamine and formic acid, and with hot, fuming sulphuric acid, carbon monoxide and hydroxylamine sulphate.

One of its hydrogen atoms is readily replaceable by metals; with alcoholic potash solution it forms crystals of $CH_2K \cdot NO_2 + C_2H_5 \cdot OH$, the alcohol being expelled in a sulphuric acid desiccator. The mercury salt is explosive.

It is a good solvent for smokeless powders and in the proportion of 10 per cent. lowers the freezing-point of nitroglycerine to $-10°$.

DINITROMETHANE, $CH_2(NO_2)_2$, forms yellow crystals exploding at 200°. Its potassium salt, $CHK(NO_2)_2$, is obtained when hydrogen sulphide is passed into an ammoniacal solution of potassium bromodinitromethane.

TRINITROMETHANE (*Nitroform*), $CH(NO_2)_3$, is obtained as ammonium salt when trinitroacetonitrile is heated with water: $C(NO_2)_3 \cdot CN + 2H_2O = CO_2 + C(NO_2)_3 \cdot NH_4$. It forms white crystals, m.-pt. 15°, and at 100° decomposes with explosion. It dissolves in water to a yellow solution and acts as a strong acid; on reduction with tin and hydrochloric acid it gives hydrocyanic acid.

TETRANITROMETHANE, $C(NO_2)_4$, obtained by heating nitroform with concentrated sulphuric and fuming nitric acids, forms white crystals, m.-pt. 13°, and boils unchanged at 126°; it is insoluble in water, but dissolves in alcohol or ether. It is non-inflammable, has no acid reaction, and, mixed with petroleum, is used as an explosive of the Sprengel type (*see* Explosives). R. Schenck (Ger. Pat. 211,198, 1908) prepared tetranitromethane in various ways.

NITROETHANE, $C_2H_5 \cdot NO_2$, has m.-pt. 113°, and nitropropane, m.-pt. 130°. Dinitroethane has b.-pt. 185° to 186°; trinitroethane, $CH_3 \cdot C(NO_2)_3$, m.-pt. 56°, is obtained from methyl iodide and the silver salt of trinitromethane. Tetranitroethane is obtained as dipotassium derivative by treating bromopicrin with potassium cyanide; it is readily decomposed, even by cold dilute sulphuric acid. Hexanitroethane, $C(NO_2)_3 \cdot C(NO_2)_3$, was prepared in 1914 by W. Will as an explosive by treating the pure potassium salt of tetranitroethane at a temperature of 3° to 5° with concentrated sulphuric acid and then with nitric-sulphuric acid, the mass being finally heated for ten minutes at 60° to 70°, and then cooled and poured into water; when freed from acid it is obtained from ether in white crystals which have a slight camphor smell, melt at 142°, and give a yellow solution in benzene or toluene; with alcoholic soda it gives tetranitroethane, while under prolonged heating at 75° it forms yellow vapours. It is moderately resistant to shock and friction, and when mixed with hydrogenated organic compounds yields explosives of practical use although of limited stability.

Various esters of *hyponitrous*, *phosphoric*, *boric*, *silicic* acids, etc., are known.

DERIVATIVES OF HYDROCYANIC ACID

A. NITRILES. B. ISONITRILES

These compounds are formed by the substitution of the hydrogen of hydrocyanic acid by an alkyl radical, but they are not true esters, as they do not give the acid and alcohol again on hydrolysis.

A. NITRILES (or Alkyl Cyanides), are either liquid or solid, and have a pleasant, faintly garlic-like, ethereal odour. They are lighter than water, in which the first terms are soluble without undergoing change. They boil at about the same temperatures as the corresponding alcohols.

PREPARATION. 1. They are obtained by distilling a potassium alkylsulphate with potassium cyanide or with anhydrous potassium ferrocyanide, or by heating the cyanide at 180° with methyl iodide :

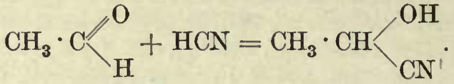
$$CH_3I + KCN = KI + CH_3 \cdot CN \text{ (\textit{methyl cyanide} or \textit{acetonitrile})}.$$

2. Distillation of ammonium salts of *monobasic acids* yields amido-compounds which, with a dehydrating agent (P_2O_5, P_2S_5 or PCl_5), give nitriles :

$$(a)\ \underset{\text{Acetic acid}}{CH_3 \cdot COOH} + NH_3 = H_2O + \underset{\text{Acetamide}}{CH_3 \cdot CO \cdot NH_2};$$

$$(b)\ CH_3 \cdot CO \cdot NH_2 - H_2O = \underset{\substack{\text{Acetonitrile or}\\ \text{Methyl cyanide.}}}{CH_3 \cdot CN.}$$

3. The higher nitriles are formed from the acid-amides containing one more carbon atom or from the primary amine containing the same number of carbon atoms, by treatment with sodium hydroxide and bromine ; or from the aldehydes which, with hydrocyanic acid, give the *nitriles of higher acids*, the so-called *cyanohydrins* or *hydroxynitriles*, liquid compounds easily saponified with regeneration of the aldehyde :



$$\underset{\text{Acetaldehyde}}{CH_3 \cdot C\begin{smallmatrix}\diagup O\\ \diagdown H\end{smallmatrix}} + HCN = \underset{\text{Ethylidenecyanohydrin}}{CH_3 \cdot CH\begin{smallmatrix}\diagup OH\\ \diagdown CN\end{smallmatrix}}.$$

PROPERTIES. When boiled with alkali or acid, or treated with superheated steam, nitriles give ammonia and an acid, from which products they may also be formed :

$$(a)\ CH_3CN + H_2O = CH_3 \cdot CO \cdot NH_2 \text{ (\textit{acetamide})};$$
$$(b)\ CH_3 \cdot CO \cdot NH_2 + H_2O = CH_3 \cdot CO \cdot OH + NH_3.$$

This reaction is of importance for the synthesis of organic acids since, starting from a given alcohol and transforming it into iodide and then into nitrile, an acid of the saturated series containing an extra carbon atom is obtained.

If the cyanide is treated with hydrogen sulphide instead of water, *thiocetamide*, $CH_3 \cdot CS \cdot NH_2$, is obtained. With hydrochloric acid, the nitriles form *chloramides* or *chlorimides*, whilst with ammoniacal bases they give *amidines* (*see later*). Nascent hydrogen converts them into *amines* : $CH_3 \cdot CN + 2H_2 = CH_3 \cdot CH_2 \cdot NH_2$ (*ethylamine*). By potassium or by gaseous hydrogen chloride the nitriles are polymerised.

ACETONITRILE (or Methyl Cyanide), $CH_3 . CN$, is found among the products of the distillation of beetroot molasses and of tar. It is soluble in water and boils at 82°.

B. ISONITRILES (Isocyanides or Carbylamines) are colourless liquids which have a faint alkaline reaction and boil at rather lower temperatures than the corresponding nitriles. They are insoluble in water, but dissolve in alcohol or ether. They have repellent odours and are poisonous. They are obtained by the interaction of alkyl iodides with silver cyanide (whilst with potassium cyanide the nitriles are obtained) :

$$C_2H_5I + AgCN = AgI + C_2H_5 \cdot NC;$$

they are also formed by treating the primary amines with chloroform and alcoholic potash (*see* p. 120) ; *also later* under Amines).

Although they are stable towards alkalis, the isonitriles are readily decomposed by water, giving formic acid and the corresponding amino-base containing one carbon atom less than the isonitrile :

$$CH_3 \cdot NC + 2H_2O = H \cdot COOH + CH_3 \cdot NH_2.$$

From the nitriles they are distinguished also by the different additive compounds which they form with halogens, hydrogen chloride, hydrogen sulphide, etc. At high temperatures certain isonitriles change into nitriles.

CONSTITUTION OF THE NITRILES AND ISONITRILES. The nitriles have the carbon atom of the cyanogen group attached to the alkyl radicle and when they are hydrolysed only the nitrogen is removed as ammonia. Acetonitrile would hence have the constitution, $CH_3 - C \equiv N$.

The isonitriles, on the other hand, readily form amino-bases with loss of an atom of carbon—that of the cyanogen group—the nitrogen remaining with the radicle. Methyl isocyanide or methylcarbylamine would hence have the formula $CH_3 - N \equiv C$.

IV. NITROGENATED BASIC ALKYL COMPOUNDS (AMINES)

If one or more of the hydrogen atoms of the ammonia molecule is replaced by one or more alkyl radicles, substances called Amines are formed; these have a basic character, which is in some cases more marked than that of ammonia itself (in the dissociation of compounds of the ammonia type, free anions, OH', are formed). They were discovered by Wurtz in 1848, and were studied systematically by A. W. Hofmann in 1850–1851. To ammonia they present other chemical analogies. They have disagreeable ammoniacal odours; with mineral acids they form white, crystalline, deliquescent salts which are extremely soluble in water and have a basic nature, the nitrogen then becoming pentavalent; for the first members of the series the electrical conductivity is very high, higher indeed than that of ammonia, since N/100 solutions are almost completely dissociated.

Like ammonia, they give, with platinum chloride, crystalline platinichlorides, *e. g.*, methylamine platinichloride, $(NH_2 \cdot CH_3, HCl)_2PtCl_4$; they also form double salts with gold chloride, $NH_2 \cdot C_2H_5, HCl, AuCl_3$. They precipitate heavy metals from solutions of their salts, and, in excess, sometimes redissolve them. The first terms are gases, after which come unpleasant smelling liquids soluble in water. The higher members are odourless and insoluble in, and lighter than, water; they are soluble in alcohol and in ether.

The ammonia derivatives are deliquescent solids, and in their behaviour greatly resemble potassium hydroxide, etc. According as they contain one or more alkyl radicals, these bases are called *primary* or *aminic*, *secondary* or *iminic*, *tertiary* or *nitrilic*, *quaternary* or *ammoniacal*.

PROCESSES OF FORMATION. (*a*) By heating an alkyl halogen compound with ammonia:

(1) $NH_3 + C_nH_{2n+1}I = HI + C_nH_{2n+1}NH_2$; the halogen hydracid formed unites with the ammonia and with the amine, converting these partly into the corresponding salts; distillation with potassium hydroxide then gives: $KI + H_2O +$ the free base, $C_nH_{2n+1} \cdot NH_2$. The latter, which is partly free before treatment with potash, may in its turn react with a second molecule of the alkyl halogen compound, giving a secondary amine;

(2) $C_nH_{2n+1} \cdot NH_2 + C_nH_{2n+1}I = (C_nH_{2n+1})_2NH, HI$; the free base, which may be liberated by distilling with KOH, reacts with a third molecule of the alkyl halogen compound, yielding a tertiary amine;

(3) $(C_nH_{2n+1})_2NH + C_nH_{2n+1}I = (C_nH_{2n+1})_3N, HI$. Finally, the tertiary base, which remains free or may be liberated, reacts with a fourth molecule of the halogen derivative, giving the salt of the quaternary base;

(4) $(C_nH_{2n+1})_3N + C_nH_{2n+1}I = (C_nH_{2n+1})_4NI$, which is no longer a crystalline ammonia base and is not decomposed by potassium hydroxide, being more energetic than the latter; the hydrogen iodide formed unites with the amines if such are still present. When heated, the iodide of the quaternary base is converted back into the tertiary base and alkyl iodide, whilst with

silver hydroxide it gives the corresponding solid alkylammonium hydroxide. In this general reaction, the four bases are always formed together, although more of one or another is obtained according to the nature of the alkyl group, the temperature, the duration of the reaction, and the quantity of ammonia present.

The separation of the bases in this mixture is not easy, and when these are present as salts, distillation with potassium hydroxide yields the primary, secondary, and tertiary amines, whilst the quaternary ammonium compound remains unchanged. The three bases or the corresponding salts are separated partly by crystallisation or by fractional distillation, or, better, by means of *ethyl oxalate*, $C_2O_2(C_2H_5O)_2$, which gives solid or liquid oxamides [*e. g.*, *solid dimethyloxamide*, $C_2O_2(NH \cdot CH_3)_2$ and the ethyl ester of *dimethyloxaminic acid*, $C_2H_2(OC_2H_5) \cdot N(CH_3)_2$, which boils at 243° and is soluble in water, alcohol or ether].

Amines may also be prepared by the following reactions:

(*b*) By the action of potassium hydroxide on alkyl isocyanates, *e. g.*, *ethyl isocyanate*, $C_2H_5NCO + 2KOH = K_2CO_3 + C_2H_5 \cdot NH_2$;

(*c*) By reducing nitro-compounds, nitrites, oximes, or hydrazones with nascent hydrogen.

(*d*) Primary amines may be obtained by heating the ethylnaphthylamines with caustic soda, and secondary amines in the same way from nitrosodialkylanilines.

PROPERTIES. The amines do not undergo hydrolysis and are resistant to the action of acids, alkalis, and, to some extent, oxidising agents. The hydrogen combined with the nitrogen of amines may be replaced not only by alkyl groups (*see above*), but also by acid radicals (*e. g.*, by *acetyl*, $CH_3 \cdot CO^{\cdot}$) and mixed amines with alkyl and acidic groups may also be obtained. A characteristic and sensitive reaction of the *primary amines* is that with chloroform in presence of alkali, which gives rise to the unpleasant-smelling isonitriles: $CHCl_3 + CH_3 \cdot NH_2 + 3KOH = CH_3 \cdot NC + 3KCl + 3H_2O$. In alcoholic solution the primary and secondary bases form, with carbon disulphide, derivatives of thiocarbaminic acid, and only when these are derived from the primary bases can isothiocyanates be obtained. It is easier to distinguish (and separate) primary, secondary, and tertiary amines by their reactions with nitrous acid. When a hydrochloric acid solution of the mixture is treated with a concentrated solution of sodium nitrite, the primary amine yields the corresponding alcohol (soluble in water), with evolution of nitrogen:

$$C_nH_{2n+1}NH_2 + NOOH = H_2O + N_2 + C_nH_{2n+1}OH.$$

The secondary amines give oily *nitrosamines*, almost insoluble in water: $(C_nH_{2n+1})_2NH + NOOH = H_2O + (C_nH_{2n+1})_2N \cdot NO$; with feeble reducing agents, the nitrosamine is transformed into a *hydrazine*, whilst with more energetic reducing agents or with concentrated hydrochloric acid the secondary amine is regenerated, showing that the nitrous residue NO is joined to the iminic nitrogen and not to the carbon. The tertiary amine does not react with nitrous acid and is hence left unchanged in the solution, from which it may be obtained by distillation in presence of caustic soda.

Finally, the three classes of amines may be distinguished by the quantities of methyl iodide with which they react to produce the final quaternary base (*see preceding page*), with generation of greater or less quantities of ionisable compounds (titratable HI).

METHYLAMINE, $CH_3 . NH_2$, is found ready formed in certain plants, *e. g.*, in the dog-mercury weed (*Mercurialis perennis*). It is formed in the distillation of wood and occurs in beetroot and bone residues and in herring brine. It is prepared from methyl chloride and ammonia, the resulting hydrochloride being separated from the ammonium chloride by dissolving the former in a little water (the ammonium chloride is less soluble), filtering by suction and crystallising the filtrate with the help of ammonia; the secondary amine formed at the same time is separated as nitroso-derivative, which with concentrated hydrochloric acid regenerates the base. Plöchl prepares methylamine by heating a mixture of formaldehyde with one-half of its weight of ammonium chloride. It is a gas like ammonia (but, unlike this, burns in the air) and precipitates various metallic salts, but, when added in excess, does not dissolve nickel and cobalt hydroxides; it is more highly basic and more soluble in water (1 vol. dissolves 1150 vols. at 12·5° and 959 vols. at 25°) than ammonia, and has a strong odour of ammonia and rotten fish. It becomes liquid at − 7° and at − 11° has the sp. gr. ·0699. It is formed by the action of NaOH and Br on acetamide, and also by the reduction of chloropicrin (*see* p. 236). Its *hydrochloride*, $CH_3 \cdot NH_2,HCl$, m.-pt. 225°, is a crystalline, deliquescent substance extremely soluble in alcohol. With aluminium sulphate its sulphate forms an alum containing $24H_2O$.

DIMETHYLAMINE, $(CH_3)_2NH$, is a liquid boiling at + 7°, and is formed, together with acetic acid, in the distillation of wood.

TRIMETHYLAMINE, $(CH_3)_3N$, is a gas which liquefies at + 3°, and has an intense odour of rotten fish. It is found in various plants (*Arnica montana*, shoots of the pear-tree, etc.), and in herring brine. It is formed by the decomposition of betaïne during the distillation of beetroot molasses (p. 117).

ETHYLAMINE, $C_2H_5 \cdot NH_2$, may be prepared as follows: 30 parts of ethyl alcohol are saturated in the cold with ammonia and the liquid heated in an autoclave at about 55° with 8 parts of liquid ammonia and 10 parts of ethyl chloride. When the vigorous phase of the reaction is at an end, the water-bath surrounding the autoclave is brought to boiling, which is maintained for four to five hours. After cooling, the excess of ammonia is allowed to escape and is used to saturate the alcohol for a succeeding operation. The residue in the autoclave is neutralised with hydrochloric or sulphuric acid and the salts separating on concentration filtered off by suction, dried and extracted with alcohol (which does not dissolve the mineral salts). After evaporation of the alcohol, the mixed bases are liberated by means of alkali and are fractionated in a column 4 metres in height. The bulk of the product is diethylamine, the ethylamine remaining in solution at a concentration of 15 to 20 per cent.

DIETHYLAMINE (and, similarly, dimethylamine) is now often prepared by decomposing paranitrosodiethylaniline (as hydrochloride) with boiling 5 per cent. caustic soda solution (in the proportion of 1 : 20), the base distilling over being dissolved in hydrochloric acid. The yield is almost theoretical, and the paranitrosophenol remaining in the yellow solution may be used for making para-aminophenol.

ETHYLAMINE is a liquid, b.-pt. + 19°, and smells strongly of ammonia, which it surpasses in basicity. It dissolves very readily in water with generation of heat. It dissolves aluminium hydroxide (like methylamine, but unlike ammonia) and to a small extent cupric hydroxide, but not ferric or cadmium hydroxide.

DIETHYLAMINE, $(C_2H_5)_2NH$, is a liquid, b.-pt. 56°, and does not dissolve zinc hydroxide.

TRIETHYLAMINE, $(C_2H_5)_3N$, is an oily liquid which precipitates metals from their salts, but does not redissolve the precipitates. It has a strongly alkaline reaction and boils at 89°. It is extremely soluble in cold water, but above 20° it becomes completely insoluble, separating from the water in an oily layer.

A group of nitrogen compounds which may be considered as formed by the condensation of ammonia (*hydrazine*, *azoimide*, *hydroxylamine*, etc.) has been already mentioned in Vol. I., p. 376. The alkyl derivatives of hydroxylamine, $NH_2 \cdot OH$, are divided into two groups: *α-alkylhydroxylamines*, in which the alkyl replaces the hydroxylic hydrogen, $NH_2 \cdot OR$, and which hence have an ether character and do not reduce Fehling's solution; and *β-alkylhydroxylamines*, in which the alkyl radical replaces an amino-hydrogen and is therefore joined to the nitrogen, R—NH—OH; these reduce Fehling's solution even in the cold and on energetic reduction yield primary amines.

Also the **Alkylhydrazines**, $RNH \cdot NH_2$, $R_2N \cdot NH_2$, etc., unlike amines, reduce Fehling's solution in the cold and give characteristic reactions with aldehydes and ketones.

The **Diazo-compounds** of the methane series are of slight importance, whilst those of the aromatic series are a very important class of compounds; the former differ from the latter in that the characteristic divalent nitrogen group, —N = N—, has its valencies saturated by *only one* carbon atom. They may be obtained by diazotising, by means of nitrous acid, aliphatic amines with the amino-group united to a carbon atom, the other valencies of which are saturated by a carbonyl (CO) or cyanogen group and by at least one hydrogen atom.

Diazomethane, CH_2N_2, which is a yellow, odourless, poisonous gas, is prepared from hydroxylamine and dichloromethylamine, or by the action of an alkali on *nitrosomethylurethane*, $CH_3 \cdot N(NO) \cdot CO \cdot OC_2H_5$. Oxidation of aromatic hydrazones (*see* p. 246; *also* Monoses) yields *diphenyldiazomethane* and similar compounds.

V. PHOSPHINES, ARSINES, AND ALKYL METALLIC COMPOUNDS

Like ammonia, the hydrogen derivatives of phosphorus, arsenic, antimony, etc., give rise to alkyl compounds which have very feebly basic characters and very unpleasant odours.

1. **PHOSPHINES.** These are gases or colourless liquids with repulsive odours. Their basic properties and their stability towards water become more marked as the number of alkyl groups increases. They are readily oxidisable with nitric acid, the remaining hydrogen atoms of the PH_3 being transformed into hydroxyl groups. The quaternary phosphonium bases are very strongly basic, and, unlike the corresponding ammonium bases, they lose an alkyl group in the form of a saturated hydrocarbon when heated, the residue being a *trialkylphosphonium oxide*.

$C_nH_{2n+1}PH_2$	$(C_nH_{2n+1})_2PH$	$(C_nH_{2n+1})_3P$	$(C_nH_{2n+1})_4P \cdot OH$
Primary phosphine	Secondary phosphine	Tertiary phosphine	Tetralkylphosphonium hydroxide

$C_nH_{2n+1}PO(OH)_2$	$(C_nH_{2n+1})_2PO \cdot OH$	$(C_nH_{2n+1})_3PO$
Alkylphosphonic acid	Dialkylphosphonic acid	Trialkylphosphine oxide

The primary and secondary phosphines are formed by heating phosphonium iodide with alkyl iodides and zinc oxide, whilst the tertiary phosphines and phosphonium derivatives are obtained from hydrogen phosphide, PH_3, and alkyl halogen compounds.

2. **ARSINES.** Well-known primary and secondary compounds are: *methylarsenic dichloride*, CH_3AsCl_2 (liquid, b.-pt. 135°); *dimethylarsenic chloride*, $(CH_3)_2AsCl$ (b.-pt. 100°); *dimethylarsine*, $(CH_3)_2AsH$ (b.-pt. 36°); *dimethylarsenic acid* or *cacodylic acid*, $(CH_3)_2AsO \cdot OH$, etc. The tertiary arsines are obtained by the action of sodium arsenide, $AsNa_3$, on alkyl iodides:

$$3C_2H_5I + AsNa_3 = 3NaI + As(C_2H_5)_3;$$

they are liquids slightly soluble in water, with which they do not form bases. The *quaternary arsonium compounds, e.g.*, $(CH_3)_4AsI$ (*tetramethylarsonium iodide*), obtained from the tertiary arsines and alkyl iodides, are, however, very energetic and are able to give, with moist silver oxide, *tetramethylarsonium hydroxide*. The derivatives of *cacodyl*

$$[(CH_3)_2As - As(CH_3)_2]$$

were studied by Bunsen (1837–1843), who obtained *cacodyl oxide*,

$$(CH_3)_2As \cdot O \cdot As(CH_3)_2,$$

by distilling arsenic trioxide with potassium acetate (this reaction serves as a delicate test for acetates in mixtures):

$$As_2O_3 + 4CH_3 \cdot COOK = 2CO_2 + 2K_2CO_3 + [As(CH_3)_2]_2O.$$

With hydrochloric acid, cacodyl oxide gives *cacodyl chloride*, $(CH_3)_2AsCl$.

Many of these cacodyl compounds are liquids which ignite in the air and have nauseating odours; the cacodyl behaves like a true electro-positive element.

3. Various alkyl derivatives are known of *antimony* (*stibines*), *boron*, *silicon*, *bismuth*, *tin*, etc., but these are of little practical importance.

4. **ALKYLMETALLIC (Organometallic) DERIVATIVES.** These are obtained from various metallic chlorides or from the metals themselves (Zn, Hg, Mg, Al, etc.) by the action of halogen derivatives of the hydrocarbons.

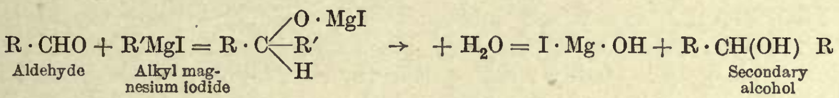
They are generally colourless liquids with low boiling-points, and some of them are violently decomposed by water and ignite in the air. Of importance for many organic syntheses are the *zinc-alkyls* (*see* pp. 33, 125).

ZINC METHYL : $Zn(CH_3)_2$, is a colourless, highly refractive liquid, sp. gr. 1·39, b.-pt. 46°, and has an intense, repulsive odour; it ignites in the air, forming zinc oxide, and with water gives methane and zinc hydroxide. It is formed in two phases, as follows, and is separated by distillation:

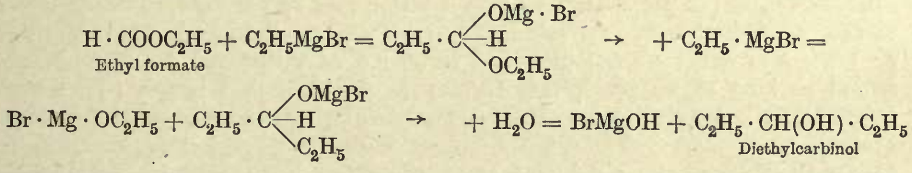
(*a*) $CH_3I + Zn = Zn(CH_3)I$ (*zinc methyl iodide*, solid);
(*b*) $2Zn(CH_3)I = ZnI + Zn(CH_3)_2$.

GRIGNARD'S REACTION. Mention has already been made of the use of this reaction in synthesising the saturated hydrocarbons (p. 33). One molecule of a monohalogenated (Br or I) compound, in presence of absolute ether, combines with an atom of magnesium: $Mg + C_2H_5Br = C_2H_5MgBr$ (*ethyl magnesium bromide*), and with compounds containing several carbon atoms there is always formed, as a secondary product, a saturated hydrocarbon. The ether probably takes part in the reaction, forming an intermediate product, $C_2H_5\cdot Mg\cdot Br[(C_2H_5)_2O]$.

The latter, and also the alkyl magnesium halogen compounds, when dissolved in ether, are highly reactive and form additive compounds with aldehydes, ketones, and even esters of mono- and poly-basic carboxylic acids; with water these additive compounds then give the corresponding *secondary* and *tertiary alcohols*, the reaction occurring in the following two phases (R = alkyl):



$$\underset{\text{Aldehyde}}{R\cdot CHO} + \underset{\text{Alkyl magnesium iodide}}{R'MgI} = R\cdot C\!\left\langle\begin{array}{l}O\cdot MgI\\ R'\\ H\end{array}\right. \rightarrow + H_2O = I\cdot Mg\cdot OH + \underset{\text{Secondary alcohol}}{R\cdot CH(OH)\;R}$$

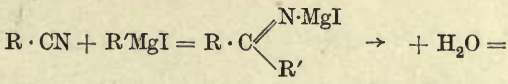


$$\underset{\text{Ethyl formate}}{H\cdot COOC_2H_5} + C_2H_5MgBr = C_2H_5\cdot C\!\left\langle\begin{array}{l}OMg\cdot Br\\ H\\ OC_2H_5\end{array}\right. \rightarrow + C_2H_5\cdot MgBr =$$

$$Br\cdot Mg\cdot OC_2H_5 + C_2H_5\cdot C\!\left\langle\begin{array}{l}OMgBr\\ H\\ C_2H_5\end{array}\right. \rightarrow + H_2O = BrMgOH + \underset{\text{Diethylcarbinol}}{C_2H_5\cdot CH(OH)\cdot C_2H_5}$$

If esters of other monobasic acids are used instead of a formic ester, tertiary alcohols are obtained, whilst esters of dibasic acids give dihydric alcohols. Hence, by means of the *Grignard reaction, the carboxylic oxygen of any acid* (starting from the corresponding ester) *is ultimately replaced by two alkyl residues.* Similar behaviour is shown by acid chlorides and anhydrides, which also contain carbonylic oxygen (—CO—).

With nitriles, *ketonimides* and *ketones* are obtained:



$$R\cdot CN + R'MgI = R\cdot C\!\left\langle\begin{array}{l}N\cdot MgI\\ R'\end{array}\right. \rightarrow + H_2O =$$

$$IMgOH + R\cdot C(:NH)\cdot R' \rightarrow + H_2O = NH_3 + R\cdot CO\cdot R' \text{ (ketone).}$$

Further, with dry CO_2, alkyl magnesium compounds give organic acids:

$$R'MgI + CO_2 = R'\cdot COOMg\cdot I \rightarrow + HX = IMgX + R'\cdot COOH \text{ (acid).}$$

Other most varied organic syntheses have been rendered possible of late years by the Grignard reaction.

VI. ALDEHYDES AND KETONES: $C_nH_{2n}O$

The elimination of two atoms of hydrogen by means of an oxidising agent (*e. g.*, potassium dichromate and dilute sulphuric acid, or sometimes even the oxygen of the air) from a primary or secondary alcohol yields an aldehyde or a ketone: $R\cdot CH_2\cdot OH + O = H_2O + R\cdot CHO$ (*aldehyde*), or

$$R\cdot CH(OH)R' + O = H_2O + R\cdot CO\cdot R' \text{ (\textit{ketone}).}$$

The aldehydes have a strong reducing action, as they fix oxygen and become converted into acids with the same numbers of carbon atoms, whilst the ketones resist oxidising agents, and, if these are very energetic, are oxidised to acids containing fewer carbon atoms than the original ketones.

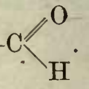
(*a*) ALDEHYDES

The first members of this series are neutral liquids with pronounced and often disagreeable odours (formaldehyde is a gas) and are soluble in water, whilst the higher ones gradually become solid and insoluble. Their boiling-points are much lower than those of the corresponding alcohols.

The aldehydes are *formed* when a calcium or barium salt (or even two salts) of a monobasic organic acid is dry distilled with calcium or barium formate (reducing agent): $(R \cdot COO)_2Ca + (H \cdot COO)_2Ca = 2CaCO_3 + 2R \cdot CHO$.

They are also obtained on heating with water compounds containing two halogen atoms united to the same carbon atom:

$$CH_3 \cdot CHCl_2 \text{ (ethylidene chloride)} + H_2O = 2HCl + CH_3 \cdot CHO.$$

The *constitution of the aldehydes* may be deduced from their methods of formation (*e. g.*, the latter) and the characteristic aldehyde group is  $—C\begin{smallmatrix}\nearrow O \\ \searrow H\end{smallmatrix}$.

PROPERTIES. They are substances of considerable and varied reactivity. With oxidising agents they are transformed into acids, and this reducing property is readily manifested in their reduction of *ammoniacal silver nitrate solution* (22 per cent. ammonia solution and 10 per cent. of dilute silver nitrate diluted with its own volume of 10 per cent. sodium hydroxide solution; or 1 gram of silver nitrate dissolved in 30 c.c. of water and dilute ammonia added as long as no precipitate forms) or of Fehling's solution (the latter, however, is not reduced by aldehydes containing as many as 8 or 9 carbon atoms).

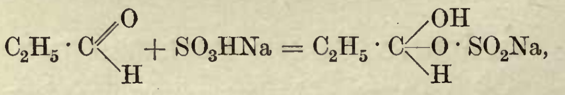
In their turn, the aldehydes are reconverted into the primary alcohols when reduced with nascent hydrogen; with PCl_5, they give ethylidene chlorides again.

Hydrocyanic acid, ammonia, sodium hydrogen sulphite, and sometimes alcohol and acetic anhydride (also the alkyl magnesium halogen compounds: *see above*, Grignard's Reaction) form characteristic *additive products* with the aldehydes:

$$CH_3 \cdot CHO + 2C_2H_5 \cdot OH \text{ (+ a little HCl)} = H_2O + CH_3 \cdot CH(OC_2H_5)_2 \text{ (\textit{acetal})}$$

which is an ether of the hypothetical glycol (dihydric alcohol), $CH_3 \cdot CH(OH)_2$; the latter, however, does not exist in the free state, since *two hydroxyl groups cannot remain joined to one and the same carbon atom*, excepting in the case of *chloral hydrate* (*see later*) and a very few other substances.[1]

They combine with sodium and ammonium bisulphites (very concentrated solutions) forming crystalline *bisulphite compounds* soluble in water and slightly so in alcohol:



$$C_2H_5 \cdot C\begin{smallmatrix}\nearrow O \\ \searrow H\end{smallmatrix} + SO_3HNa = C_2H_5 \cdot C\begin{smallmatrix}\nearrow OH \\ -O \cdot SO_2Na, \\ \searrow H\end{smallmatrix}$$

and these compounds, when heated with dilute acid or with alkali (even Na_2CO_3), liberate the aldehyde again. This reaction hence renders possible the separation of aldehydes from other substances.

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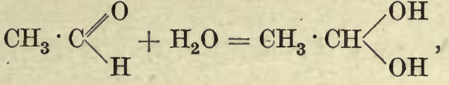
[1] *See* Table on opposite page.

The aldehydes combine with ammonia, forming crystalline *aldehyde-ammonias* soluble in water and slightly so in alcohol but insoluble in ether, for example, $CH_3 \cdot CH(OH)(NH_2)$, which gives the aldehyde again when heated with a dilute acid. But formaldehyde, with ammonia, readily forms polymerised derivatives, *e. g.*, *hexamethylenetetramine*, $(CH_2)_6N_4$ (*see later*).

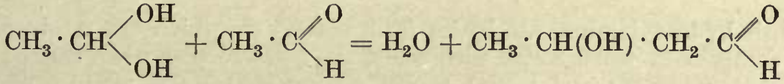
With hydrocyanic acid they form *cyanohydrins* (p. 238).

An interesting change is the *aldol condensation*, that is, the condensation of 2 mols. of an aldehyde brought about by prolonged heating with dilute mineral acids, dilute alkalis, or even aqueous solutions of sodium acetate Possibly a molecule of water is first added to one of the aldehydes :



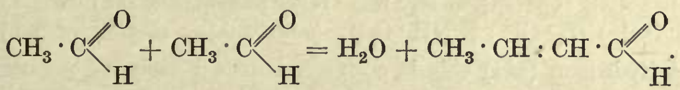
$$CH_3 \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array} + H_2O = CH_3 \cdot CH\begin{array}{l} \diagup OH \\ \diagdown OH \end{array},$$

this hypothetical hydrate then condensing with another molecule of aldehyde, with separation of water and formation of a hydroxyaldehyde (*aldol*) :



$$CH_3 \cdot CH\begin{array}{l} \diagup OH \\ \diagdown OH \end{array} + CH_3 \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array} = H_2O + CH_3 \cdot CH(OH) \cdot CH_2 \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array}$$

(*β-hydroxybutyraldehyde*). These aldols in their turn readily lose a molecule of water, forming an unsaturated aldehyde, which may also be obtained directly (*aldehyde condensation*) by heating the original aldehyde with a dehydrating agent such as zinc chloride :



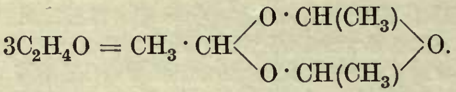
$$CH_3 \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array} + CH_3 \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array} = H_2O + CH_3 \cdot CH : CH \cdot C\begin{array}{l} \diagup O \\ \diagdown H \end{array}.$$

The aldehydes, especially form-, acet-, and prop-aldehydes, etc., exhibit a tendency to *polymerise*, in the mere presence of a little hydrochloric or sulphuric acid, sulphur dioxide, zinc chloride, etc. Acetaldehyde, for example, gives

DERIVATIVES OF ACETALS

Name	Formula	Boiling-point	Specific gravity
ALKYL DERIVATIVES			
Methylal . . .	$CH_2(OCH_3)_2$	41·3°–41·7° (749·8 mm.)	0·862 (18°)
Diethylmethylal . .	$CH_2(OC_2H_5)_2$	87°	0·834 (20°)
Dipropylmethylal .	$CH_2(OC_3H_7)_2$	136°	0·834 (20°)
Diisopropylmethylal .	$CH_2(OC_3H_7)_2$	118°	0·831 (20°)
Diisobutylmethylal .	$CH_2(OC_4H_9)_2$	164°	0·824 (20°)
Diisoamylmethylal .	$CH_2(OC_5H_{11})_2 + H_2O$	206°	0·835 (20°)
Dihexylmethylal . .	$CH_2(OC_6H_{13})_2$	174°-175°	0·822 (15°)
Dioctylacetal . .	$CH_3 \cdot CH(OC_8H_{17})_2$	289°	0·848 (15°)
Dimethylacetal . .	$CH_3 \cdot CH(OCH_3)_2$	63°	0·865 (22°)
Diethylacetal . .	$CH_3 \cdot CH(OC_2H_5)_2$	102·9°	0·831 (20°)
Dipropylacetal . .	$CH_3 \cdot CH(OC_3H_7)_2$	147°	0·825 (22°)
Diisobutylacetal . .	$CH_3 \cdot CH(OC_4H_9)_2$	170°	0·816 (22°)
Diisoamylacetal . .	$CH_3 \cdot CH(OC_5H_{11})_2$	211°	0·835 (15°)
ACID DERIVATIVES			
Methylenediacetate .	$CH_2(O \cdot CO \cdot CH_3)_2$	170°	—
Ethylenediacetate .	$CH_3 \cdot CH(O \cdot CO \cdot CH_3)_2$	169°	1·073 (15°)
Ethylenedipropionate .	$CH_3 \cdot CH(O \cdot CO \cdot C_2H_5)_2$	192°	1·020 (15°)
Ethylenedibutyrate .	$CH_3 \cdot CH(O \cdot CO \cdot C_3H_7)_2$	215°	0·985 (15°)
Ethylenediisovalerate .	$CH_3 \cdot CH(O \cdot CO \cdot C_4H_9)_2$	225°	0·947 (15°)

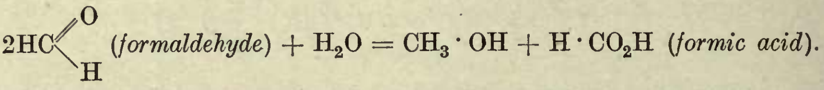
two isomerides: *paraldehyde*, m.-pt. 10°, b.-pt. 124°, and *metaldehyde*, which sublimes at 100°:



$$3C_2H_4O = CH_3\cdot CH\left\langle\begin{matrix} O\cdot CH(CH_3) \\ O\cdot CH(CH_3) \end{matrix}\right\rangle O.$$

These no longer react with ammonia, sodium bisulphite, silver nitrate, and hydroxylamine, but they yield the aldehyde again when distilled in presence of a small quantity of dilute sulphuric acid.

With alkalis, even dilute alkalis, many aldehydes, especially the more simple ones of the fatty series, resinify, whilst some give rise to an alcohol and an acid:



$$2HC\left\langle\begin{matrix} O \\ H \end{matrix}\right. \text{ (formaldehyde)} + H_2O = CH_3\cdot OH + H\cdot CO_2H \text{ (formic acid)}.$$

With halogens the aldehydes give substitution products, and with hydrogen sulphide various complex products (*thioaldehydes*, etc.) with characteristic odours.

With hydroxylamine, aldehydes form *aldoximes*, which are resolved into their components when boiled with acids, and yield nitriles when treated with dehydrating agents: $CH_3\cdot CHO + NH_2\cdot OH = H_2O + CH_3\cdot CH:N\cdot OH$.

A similar action is exhibited by the hydrazines (as hydrochloride or acetate in acetic acid solution containing sodium acetate; the most suitable is phenylhydrazine), which give characteristic, stable, and often crystalline compounds, termed *hydrazones:*

$$CH_3\cdot CHO + C_2H_5\cdot NH\cdot NH_2 \text{ (ethylhydrazine)} =$$
$$H_2O + CH_3\cdot CH:N\cdot NH\cdot C_2H_5 \text{ (acetaldehyde ethylhydrazone)};$$

by nascent hydrogen (4H) this is converted into 2 mols. of primary amine:

$$2CH_3\cdot CH_2\cdot NH_2.$$

With oxidising agents the phenylhydrazone gives *diphenyldiazomethane*, $(C_6H_5)_2\,C:N_2$.

Characteristic of the aldehydes is also the formation of crystalline *semicarbazones* by the action of the hydrochloride of *semicarbazide*, $NH_2\cdot CO\cdot NH\cdot NH_2$ (obtained by the interaction of potassium cyanate and hydrazine hydrate):

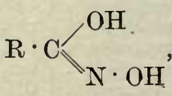
$$R\cdot CHO + NH_2\cdot CO\cdot NH\cdot NH_2 = H_2O + R\cdot CH:N\cdot NH\cdot CO\cdot NH_2.$$

Both the hydrazones and semicarbazones serve for the separation of the aldehydes from other substances and for their quantitative determination.

From aqueous liquids aldehydes are separated by means of *metanitrobenzhydrazide*, with which they form insoluble condensation products.

A gaseous mixture containing as little as 0·5 mgrm. of formaldehyde per 100 c.c. precipitates grey, metallic mercury in the cold when passed through Federer's mercuric solution.

Finally a characteristic qualitative reaction which is given generally by the aldehydes and is very sensitive is that of Schiff. It consists in shaking the liquid to be tested with a solution (0·02 per cent.) of fuchsine previously decolorised by a current of sulphur dioxide. Traces of an aldehyde produce a reddish-violet coloration (it is uncertain if *pure* ketones also give this reaction).

Another reaction characteristic of the aldehydes and not given by ketones is that with benzosulphinehydroxamic acid or with *nitrohydroxylaminic acid*, $OH\cdot NO:N\cdot OH$, which forms *hydroxamic acids*,  $R\cdot C\left\langle\begin{matrix} OH \\ N\cdot OH \end{matrix}\right.$, the latter producing a cherry-red coloration with ferric chloride.

FORMALDEHYDE (or Methanal), $H \cdot CHO$, was discovered by A. W. Hofmann in 1868 by passing air saturated with methyl alcohol vapour over a red-hot platinum spiral. Kekulé obtained it pure in 1892.

If it occurs out of contact with air, the oxidation of methyl alcohol in presence of the catalyst is endothermic: $CH_3 \cdot OH = CH_2O + H_2 - 28$ Cals.; as a secondary reaction part of the aldehyde may decompose with formation of CO and H_2 and development of 3·6 Cals. On the large scale it is hence necessary to prolong the heating so as to maintain the most suitable temperature for the copper catalyst (500° to 600°), which rapidly loses its activity under such conditions. In presence of oxygen (theoretically 200 litres of air measured at 15° per 100 grams of methyl alcohol), however, the reaction is exothermic, but the reaction, $CH_3 \cdot OH + O = CH_2O + H_2O + 30{\cdot}2$ Cals., which should be the primary reaction, is not verified. It seems rather that the copper catalyst gives an oxide, which with the carbon monoxide and hydrogen formed (according to the first equation) would regenerate the copper with formation of H_2O and CO_2 and generation of sufficient heat to cause the reaction, once started, to proceed without further heating.

Formaldehyde is a gas which irritates the eyes and liquefies at − 21° to a mobile, colourless liquid having the sp. gr. 0·8153 (or 0·9172 at − 80°) and solidifying at − 92°. It is very soluble in alcohol or water (52·5 per cent.), and is placed on the market in the form of 40 per cent. (by vol. or 36 per cent. by weight) aqueous solution [1] under the name of *formalin* or *formol;* this aqueous solution gradually undergoes change (it lasts at most six months), so that the commercial product often contains 12 to 15 per cent. of methyl alcohol, this being added to prevent separation of polymerised compounds (*see later*). The heat of formation of the gaseous aldehyde is 25 Cals., the heat of solution in water being 15 Cals.

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[1] The concentrations of commercial aqueous solutions of formaldehyde may be deduced from the specific gravities by means of the following table (*Auerbach*, 1905):

Sp. gr. at $\frac{18^\circ}{4^\circ}$	Grams of CH_2O in 100 c.c. of solution	Grams of CH_2O in 100 grams of solution
1·0054	2·24	2·23
1·0090	3·50	3·45
1·0126	4·66	4·60
1·0172	6·51	6·30
1·0218	8·37	8·0
1·0311	11·08	10·74
1·0410	14·15	13·59
1·0568	19·89	18·82
1·0719	25·44	23·73
1·0853	30·17	27·80
1·1057	37·72	34·11
1·1158	41·87	37·53

If the aldehyde is pure and leaves no residue, the percentage by volume, if greater than 23, should be increased by about 5.

The analysis of commercial formalin is based on the following reaction of Blank and Finkenbeiner: $2CH_2O + 2NaOH + H_2O_2 = H_2 + 2H_2O + 2H \cdot CO_2Na$. Three grams of the formaldehyde solution is poured into a long-necked flask containing 25 c.c. of 2N-caustic soda solution (free from carbonates), the liquid being mixed and 50 c.c. of hydrogen peroxide solution (neutralised or of known acidity) carefully added, 3 minutes being taken to make this addition. After seven to eight minutes, the excess of alkali remaining is titrated with 2N-sulphuric acid. With every cubic centimetre of the 2N-alkali that has reacted corresponds 0·06 gram of formaldehyde. Litmus purified several times with alcohol should be used as indicator.

The estimation of the aldehyde may also be carried out with ammonia (*see succeeding Note*).

Bräutigam (1910) suggested the determination of formaldehyde by adding to it excess of clear calcium hypochlorite solution. After a time the solution deposits calcium carbonate, which is filtered, washed, and weighed; 1 mol. of $CaCO_3$ corresponds with 1 mol. of formaldehyde.

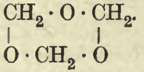
To determine the *methyl alcohol* which may be present, 5 c.c. of the solution, diluted with 100 c.c. of water, is distilled with an excess of ammonia (about 10 c.c. of concentrated ammonia), 50 c.c. of the distillate being collected in a 100 c.c. flask and made up to volume with water. The methyl alcohol in 5 c.c. of this solution, which contains only negligible traces of formaldehyde, is determined by the iodine method (*see* p. 129).

A question which has been under discussion for many years is the possible formation of formaldehyde as the first product in the natural synthesis of carbohydrates (*see* Sugar) in the leaves of plants, from carbon dioxide under the influence of chlorophyll.

Numerous sensitive reagents have been employed to detect microscopically the transitory formation of formaldehyde in *living* leaves, but almost all these reagents are poisonous to plants and no decisive results have been obtained, even those of Pollacci (1907), who distilled the leaves with water and tested for formaldehyde in the distillate, being doubtful. Schryver (1910) has succeeded in establishing the formation of aldehyde in green plants in sunlight, by making use of a very sensitive reagent (detecting 1 part of aldehyde per million) consisting of a solution of phenylhydrazine, potassium ferricyanide, and hydrochloric acid; this reagent gives a red coloration with formaldehyde or with the methylene derivative which chlorophyll would form with the aldehyde.

Angelico and Catalano (1913) have demonstrated the presence of formaldehyde in the juices of green plants by means of a very sensitive reagent, *atractylin*, which is the active component of the glucoside of *Atractylis gummifera*. Treatment of a trace of atractylin with two or three drops of concentrated sulphuric acid yields a yellow coloration, which changes to violet and then to blue on addition of a drop of a very dilute solution of formaldehyde; this reaction appears to be specific for formaldehyde.

PROPERTIES. Formaldehyde polymerises to a white buttery mass of *paraformaldehyde*, $6CH_2O + H_2O$, which is also formed in soft flocks when the aqueous aldehyde is evaporated. Paraformaldehyde dissolves in hot water and then shows all the properties of a solution of formaldehyde. Treatment of formaldehyde solution with concentrated sulphuric acid results in the separation of a white crystalline mass of *polyoxymethylene* (improperly termed trioxymethylene), of which four modifications (α—, β— γ— and δ—oxymethylenes) are known; these are insoluble in alcohol or ether, have m.-pts. 165° to 172°, and behave like formaldehyde when heated or in aqueous solution. True α-trioxymethylene, produced under definite conditions (*e. g.*, with a trace of sulphuric acid) from formaldehyde vapour in the hot, forms white, pliable, acicular, highly refractive crystals, m.-pt. 63°, which sublime readily and are soluble in water, alcohol, or ether; its true constitution is



$$\begin{array}{l} CH_2\cdot O\cdot CH_2. \\ \,| \qquad\quad\;\; | \\ O\cdot CH_2\cdot O \end{array}$$

These different solid polymerides of formaldehyde yield vapour of the latter when heated, and hence serve as convenient and portable disinfectants (as pastilles), being sold under various trade names (*triformol, paraformol*, etc.).

With ammonia formaldehyde gives, not an aldehyde-ammonia, but *hexamethylenetetramine* (*urotropine*),[1] $C_6H_{12}N_4$, which is crystalline and of feebly monobasic character; this compound is used as an antifermentative to preserve milk and to fix the excess of sulphurous acid in wine (*see* note, p. 187), and medicinally as a solvent for uric acid in the treatment of uric arthritis. With hot, dilute caustic soda solution the aldehyde does not resinify, but gives methyl alcohol and formic acid (*see above*); with the concentrated alkali it yields only formic acid and nascent hydrogen, and in these conditions exerts a strong reducing action and separates Ag, Au and Hg from their salts.

Formaldehyde is one of the most active substances chemically and lends itself to many varied organic syntheses. Under the action of minimal proportions of certain alkalies, *e. g.*, lime water, it undergoes condensation to *glycollic aldehyde*, $OH\cdot CH_2\cdot CHO$, and then to formose, $C_6H_{12}O_6$, the principal component of which is *α-acrose* or inactive fructose.

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[1] This reaction was proposed by L. Legler in 1883 as a means of estimating formaldehyde in commercial solutions: $6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$; the reaction is, however, slow and the method not very accurate. F. Hermann (1911) has rendered it more rapid and exact in the following manner. Four cubic centimetres of the formalin is weighed into a 150 c.c. flask with a ground stopper, and about 3 grams of pure powdered ammonium chloride and exactly 25 c.c. of 2N-caustic soda (equivalent to 50 c.c. of normal soda) added. The flask is stoppered and shaken, and, when the mass is cool, 50 c.c. of water and 4 drops of 1 per cent. methyl orange are added and the excess of alkali titrated with normal sulphuric acid. Deduction of the volume of acid required from 50 c.c. gives the volume of soda used in liberating, from the ammonium chloride, a corresponding amount of nascent ammonia, which instantly transforms the aldehyde into hexamethylenetetramine. The latter is, however, monobasic and reacts with part of the sulphuric acid, and, in order to obtain the number of grams of formaldehyde in the quantity of formalin taken, the number of cubic centimetres of soda arrived at above must be multiplied by the factor 0·06. If the formalin be acid initially, the acidity must be determined separately by titration with soda in presence of phenolphthalein and the 50 c.c. of soda increased accordingly.

With bisulphite solution and zinc dust it yields hydrosulphite compounds (*see* Vol. I., p. 586). A characteristic and very sensitive reaction of formaldehyde is that proposed by Rimini, according to whom a mixture of phenylhydrazine hydrochloride, sodium nitroprusside, and caustic soda is coloured blue even by minimal traces of the aldehyde.

Formaldehyde gives Schiff's reaction (*see above*) even in presence of a certain amount of sulphuric acid, whilst acetaldehyde does not.

MANUFACTURE. In 1886 O. Loew replaced the platinum used as catalyst by copper, the yield of aldehyde thus obtained being 31 per cent. of the theoretical yield.

In 1908 Orloff devised a large-scale plant in which rectifying columns were used, igniters composed of heaps of platinised asbestos taking the place of the initial heating. Platinum being excluded on account of its high price and iron owing to its low yield, either silver gauze or asbestos impregnated with silver was used as catalyst, the yield being almost theoretical (Ger. Pat. 228,697; U.S. Pats. 1,067,668 and 1,100,076). The most suitable temperature for the formation of the aldehyde is about 450°, decomposition into CO and H_2 occurring if this is surpassed. The catalytic layer should not exceed a certain thickness. The methyl alcohol is used at a concentration of 90 per cent., but 98 per cent. is better, provided that not more than 1 per cent. of acetone is present. In order to obtain the proper proportion between alcohol and air (1 part of alcohol and 0·36 part of oxygen), the latter is passed through alcohol heated to about 52°; about 35 per cent. of the alcohol should distil unchanged, whilst 65 to 70 per cent. is transformed into aldehydes. An apparatus designed by Orloff and modified by F. H. Meyer is shown in Fig. 181. The vessel *2* contains a supply of air furnished by the compressor *1*, this passing gradually into the saturator *4*, where it meets a spray of alcohol from the tank *3*. By means of steam coils the saturator is kept at 52°, the air, saturated with alcohol vapour, at this temperature proceeding to the catalysing chamber *5*, in which the alcohol is partially oxidised to aldehyde. The mixture of aldehyde, alcohol, nitrogen and water vapour from *5* enters at the bottom of the rectifying column *6*, in which the temperature is regulated so that a 40 per cent. aqueous formaldehyde solution condenses; this is discharged into the separator *8*, and thence into the vessel *B*. The excess of alcohol vapour passes from the top of the column to the condenser *7*, the condensed alcohol being collected in the tank *12* and thence pumped to the tank *3*, into which a further amount of alcohol is forced by the pump *14*. The nitrogen and other gases escaping from *11* are washed with a little water in the tower *9* before being dispersed into the air; the small amount of dilute methyl alcohol thus recovered is rectified in the column *10*, from which the condensed water is discharged at *A*, while the alcohol vapour from the top of the column is condensed in *11*, the liquid flowing into the tank *12*.

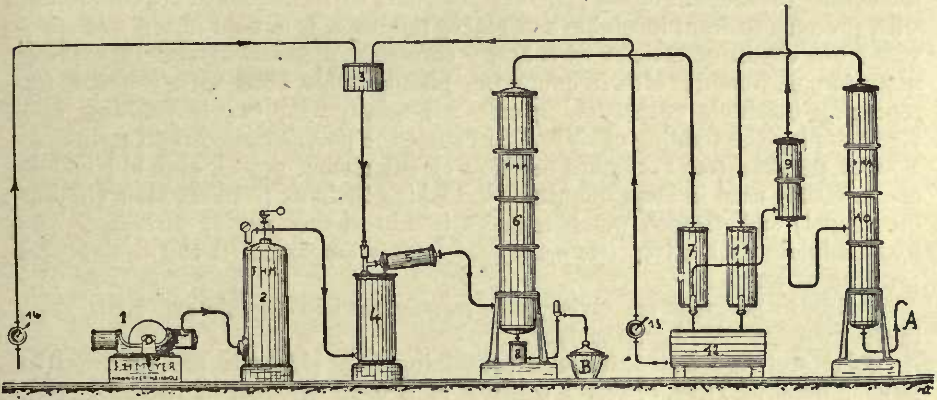

FIG. 181.

The catalyser is formed of a bundle of six copper tubes 60 cm. long and 5 cm. in diameter, fixed to tubulated plates so as to form, in the cylinder containing these tubes, a distributing chamber at the entrance, and a collecting chamber for the oxidised gases at the exit, of the tubes. At the front end of each tube is a compact roll of fine copper gauze, forming a sort of plug 11 cm. long, this being preceded by a small tuft of platinised asbestos which automatically ignites the alcohol vapour. The formaldehyde condensing in the column *6* (if the height and temperature of this are properly regulated) contains 14 per cent. of methyl alcohol, 52 per cent. of water and 40 per cent. of formaldehyde. Various modifications in the saturator have been suggested (*see* Ger. Pat. 106,495, 1898). Ignition of the alcohol vapour by means of electrical resistances in the catalysing apparatus has also been attempted (W. Löb, 1912).

Various endeavours which have been made to prepare formaldehyde from methane (*e. g.*, by mixing it with an equal volume of air and using granulated copper at 600° as catalyst) have not yet given satisfactory results (Ger. Pats. 109,014, 214,155, 286,731, etc.), the yields being very low. Further, practical success has not attended the preparation of formaldehyde, either by reducing formic acid vapour mixed with hydrogen in presence of various metals at high temperatures (Ger. Pat. 185,932, 1905), or by heating tin formate at 180° so as to decompose it into CO_2 and formaldehyde (Ger. Pat. 183,856).

USES. Formaldehyde has considerable antiseptic power, even in aqueous solution; its use in foodstuffs is prohibited. It is largely used at the present time in 1 to 3 per cent. solutions as a disinfectant in houses and for the preservation of readily putrescible substances (1 part in 2000 kills bacteria and 1 in 1000 also spores). Its vapour has an acute and penetrating odour and irritates the eyes. On account of the property possessed by formaldehyde of combining with proteins to form insoluble and stable products, it is used in the manufacture from casein of articles of a horny consistency (*galalith*) and in making imitation pegamoid; also in preparing photographic films with gelatine, for rendering insoluble or hardening coloured gelatine for textile printing, and for hastening the tanning of skins. It causes the polymerisation and resinification of phenols (*see* Formolite reaction of petroleum, pp. 71 and 91) and is consequently used in large quantities in making *baekelite* (*see* Part III: chapter on Phenol) and *neradol*, which replaces tannin in the tanning of hides. The hydrosulphite derivatives (*see above*) are largely employed in the dyeing and printing of textiles.

Owing to its great reactivity, it is largely used in organic syntheses, *e. g.*, in the manufacture of aniline dyes.

Solid and liquid disinfectants containing free aldehyde are prepared in large number. Thus, *lysoform* consists of a soap solution of formaldehyde, and mixtures or compounds of the aldehyde with sugar, oil, quinones, amines, creosote, ichthyol (*see* p. 103), ricinoleic acid (*ozoform*), etc., are also sold.

STATISTICS AND PRICES. The price of commercial 40 per cent. formaldehyde is about £40 per ton, while pure, powdered paraldehyde costs 4*s.* to 5*s.* per kilo.

Germany consumed about 500 tons of formaldehyde per annum before the war.

Italy produces it in varying amounts, as much as 60 tons per annum being sometimes made prior to the war, when the importation was about 250 tons per year.

For France the movements of the aldehyde are as follows (tons):

	1910	1914	1915	1916
Importation . .	469	391	1047	613
Exportation . .	25	16	83	33

ACETALDEHYDE (Ethanal), $CH_3 \cdot CHO$, is a colourless, mobile liquid, sp. gr. 0·801 (at 0°), b.-pt. 21°, and solidifies at −121°. It has an agreeable but suffocating odour, and it polymerises with moderate ease, giving the *paraldehyde* and *metaldehyde* (*see above*). It dissolves in water, alcohol, or ether, and is readily converted into acetic acid by oxidising agents.

It is prepared by pouring a mixture of 3 parts of 90 per cent. alcohol and 4 parts of concentrated sulphuric acid slowly into a solution of 3 parts of potassium dichromate in 12 of water, the liquid being kept cool meanwhile. The solution is then heated in a reflux apparatus on a water-bath and subsequently distilled. The mixture of alcohol, aldehyde, and acetal thus obtained is heated to 50° and the aldehyde vapour passed into cold ether. On passing ammonia into this solution, crystallised aldehyde-ammonia, $CH_3 \cdot CH(OH) \cdot NH_2$, separates; this, when pressed and distilled with dilute sulphuric acid, gives pure acetaldehyde. The *commercial aldehyde* is obtained from the foreshots of alcohol distillation, from which it is separated by simple fractional distillation.

It is of importance in many organic syntheses and in the production of silver mirrors. The price of 50 per cent. solutions before the war was 2*s.* per kilo, that of the 95 to 99 per cent. product 3*s.* 6*d.*, and that of the purest aldehyde 15*s.*[1]

METHYLAL, $H \cdot CH(OCH_3)_2$, **ACETAL**, $CH_3 \cdot CH(OC_2H_5)_2$ (*see* p. 245).

PROPALDEHYDE, $C_2H_5 . CHO$, is found among the tarry products from the distillation of wood. Valeraldehyde, $C_4H_9 \cdot CHO$, boils at 92° and begins to show a diminution in solubility in water. Normal heptaldehyde (*œnantaldehyde*), $C_6H_{13} \cdot CHO$, is found among the products of decomposition of castor-oil when this is subjected to distillation in a vacuum. Nonyl aldehyde, $C_8H_{17} \cdot CHO$, occurs in the oxidation products of oleic acid or, better, in the decomposition products of the ozonide of oleic acid (Harries, Molinari, etc.); it boils at about 192°.

CHLORAL (Trichloroethanal), $CCl_3 \cdot CHO$, is the most important halogenated derivative of the aldehydes. It is a dense liquid with a peculiar, penetrating odour and boils at 94·4°. It is prepared by passing chlorine into pure alcohol (96 per cent.) for some days, the hydrochloric acid formed being collected. At first the mass is cooled, but is afterwards heated to 60° and then to 100°, the stream of chlorine being suspended when a little of the liquid dissolves completely in water. The reaction may be accelerated by addition of a trace of iodine or ferric chloride. The final product is heated to boiling under a reflux condenser with an equal amount of concentrated sulphuric acid in a lead-lined apparatus. After evolution of hydrogen chloride has ceased, the liquid is distilled until the temperature of the vapour reaches 100°, the distillate being subsequently rectified and the fraction boiling at 94° to 97° collected separately. If this chloral is mixed with an equimolecular proportion of water it forms a crystalline mass of chloral hydrate (*see below*), which may be pressed and crystallised from chloroform, CS_2 or benzene. Chloral is also prepared electrolytically: the bath contains potassium chloride solution at 100° and is fitted with a diaphragm; alcohol is passed into the anode chamber, where chlorine is formed, and the hydrogen chloride produced at the anode (carbon) is neutralised by the potassium hydroxide formed (1 h.p.-hour yields 50 grams of chloral); the cathode is of copper.

Chloral gives the reactions of the aldehydes and is used in medicine as an anæsthetic and soporific, being first treated with water to form the crystalline **CHLORAL HYDRATE**, $CCl_3 \cdot CH{<}\begin{matrix}OH\\OH\end{matrix}$, which is readily soluble in water (m.-pt. 57°); this is one of the few compounds having two hydroxyl groups united to the same carbon atom. The crystalline alcoholates or Acetals, $CCl_3 \cdot CH(OH) \cdot OC_2H_5$ and $CCl_3 \cdot CH(OC_2H_5)_2$, corresponding with this hydrate, are known.

Chloral costs about 6*s.* per kilo.

ALDEHYDES WITH UNSATURATED RADICALS

ACRALDEHYDE (Propenal, Acroleïn, or Allyl Aldehyde), $CH_2 : CH \cdot CHO$, is formed when fats are burned, owing to loss of water by the glycerol present; a similar change takes place when glycerol is heated with potassium hydrogen sulphate or boric acid. By distillation of 200 c.c. of concentrated glycerine with 10 grams of potassium bisulphate

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[1] The *estimation* of acetaldehyde is based on the following reaction (Seyewetz and Bardin):

$$2Na_2SO_3 + 2CH_3 \cdot CHO + H_2SO_4 = Na_2SO_4 + (CH_2 \cdot CHO, NaHSO_3)_2.$$

The aldehyde is diluted to 7 to 8 per cent. and about 10 c.c. of this solution is poured into 40 c.c. of 10 per cent. pure sodium sulphite solution. After the addition of a few drops of neutralised alcoholic phenolphthalein solution the liquid is cooled to 4° to 5° and titrated with normal sulphuric acid until it is decolorised. This occurs when no further combination of aldehyde and sulphurous acid takes place. This determination is not affected by the presence of alcohol, acetal, or paraldehyde.

at 105° to 110° and rectification of the first distillate (140 to 150 c.c.), 35 c.c. of acroleïn are obtained.

Acroleïn, which may also be obtained by the oxidation of allyl alcohol, is a liquid, b.-pt. 52·4°, and has a characteristic pungent odour. When oxidised, it yields acrylic acid and, when reduced, allyl alcohol. It has all the chemical properties of the aldehydes and polymerises in the course of a few hours. With ammonia, it gives a solid, basic condensation product, soluble in water: $2C_3H_4O + NH_3 = H_2O + C_6H_9ON$ (*acroleïn-ammonia*, which gives *picoline* on distillation). Owing to its double linking, acroleïn unites with 2 mols. of sodium bisulphite, and the resulting product, when boiled with acid, gives up only one bisulphite molecule, namely, that combined with the aldehyde group.

CROTONALDEHYDE, $CH_3 \cdot CH : CH \cdot CHO$, is obtained by distilling the corresponding aldol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO$, at 140° or by the dehydrating action of zinc chloride or sodium acetate on the saturated aldehyde. It is a liquid boiling at 104° and possessing a penetrating odour, and its constitution is shown by the fact that it yields crotonic acid when oxidised with silver oxide.

CITRAL (or Geranial), $(CH_3)_2C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CHO$, is a liquid of pleasant odour, b.-pt. 229°, and occurs in many essences (of mandarin, citron, lemon, orange, and most abundantly—60 per cent.—in that of *Verbena indiana* or lemon-grass, from which it is separated by means of its bisulphite compound). It may also be obtained by the gentle oxidation of the corresponding alcohol, *geraniol*, which boils at 230°. It exists in two stereoisomeric forms, the cis- and trans-modifications. When oxidised with potassium bisulphate at 170°, citral is transformed into *cymene* (with a closed ring) with separation of water.

CITRONELLAL, $(CH_3)_2C : CH \cdot CH_2 \ CH_2 \cdot CH(CH_3) . CH_2 \cdot CHO$, is found with citral in citron oil and boils at 208°.

PROPARGYL ALDEHYDE, $CH \vdots C \cdot CHO$, is a solid, m.-pt. 60°, and is obtained from dibromoacroleïn by way of the acetal. As it contains the group $CH \vdots C$, it forms metallic derivatives (*see* pp. 110 and 112).

(*b*) KETONES (R—CO—R′)

These have the carbonyl group attached to two alcohol radicals and, if the latter are similar, are known as *simple ketones* and, if different, *mixed ketones*. The first member must contain at least three carbon atoms. They present the same cases of isomerism as the secondary alcohols, and are metameric with the aldehydes.

Up to the C_{11}-compound they are liquid and beyond that solid, but all are less dense than water. They resist feeble oxidation, but energetic oxidising agents (dichromate and dilute sulphuric acid) break the chain of the ketone at the carbonyl group, thus forming an acid with a lower number of carbon atoms: $CH_3 \cdot CO \cdot CH_3 + 4O = H_2O + CO_2 + CH_3 \cdot CO_2H$. In mixed ketones, however, the carboxyl is united mainly to the smaller alkyl radical (R or R′), but the acid with the higher alkyl is always formed to some extent. With ammonia, the action is different from that in the case of aldehydes: water is eliminated from 2 or 3 mols. of ketone and *di-* and *tri-ketonamines* (or *acetonamines*), *e. g.*, $C_6H_{13}ON$, formed. Further, the ketones do not polymerise, but they form condensation products. They do not react with ammoniacal silver solutions or with Fehling's solution, and are hence not reducing in character (difference from aldehydes).

With phosphorus pentachloride they give the corresponding dichloro-derivatives; for instance, acetone gives 2-dichloropropane, $CH_3 \cdot CCl_2 \cdot CH_3$.

On reduction, they yield secondary alcohols, and with very energetic oxidising reagents (H_2O_2, etc.) they form *characteristic* polymerised ketonic peroxides, *e. g.*, $[(CH_3)_2CO_2]_2$, $[(CH_3)_2CO_2]_3$. With ethyl orthoformate they give *acetals*, $(CH_3)_2C(OC_2H_5)_2$, and similarly with mercaptans they form **Mercaptols**, *e. g.*, $(CH_3)_2C(SC_2H_5)_2$, which, when oxidised with permanganate, gives **Sulphonal**, $(CH_3)_2C(SO_2C_2H_5)_2$ (*see* pp. 119 and 233).

Ketones, which generally contain the group $CH_3 \cdot CO \cdot$, form, with sodium bisulphite, compounds which are crystalline and hence readily separable from other substances :

$$(CH_3)_2CO + SO_3HNa = (CH_3)_2C{<}\begin{smallmatrix}OH\\SO_3Na\end{smallmatrix} \text{ (\textit{sodium acetonebisulphite}).}$$

This compound crystallises also with 1 mol. H_2O and yields acetone easily when heated with dilute soda solution.

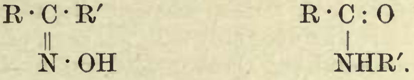
With hydrocyanic acid, ketones give the *cyanohydrins* or nitriles of higher acids : *e. g.*, $(CH_3)_2C{<}\begin{smallmatrix}OH\\CN\end{smallmatrix}$.

With hydrogen sulphide, but *only* in presence of HCl, etc., they form *trithioketones*, which on heating give simple *thioketones*.

With hydroxylamine, ketones readily form the so-called *ketoximes*, $R_2C : N \cdot OH$,[1] similar to aldoximes, and with phenylhydrazine they give phenylhydrazones, just as aldehydes do :

$$(CH_3)_2CO + NH_2 \cdot OH = H_2O + (CH_3)_2C : N \cdot OH \text{ (\textit{acetoxime}).}$$

Under certain conditions, *e. g.*, by the action of acetyl chloride, ketoximes undergo an atomic transposition by which they are converted into amides substituted in the amino-group (Beckmann rearrangement), these being tautomeric with the ketoximes :



$$\begin{array}{c} R \cdot C \cdot R' \\ \| \\ N \cdot OH \end{array} \qquad \begin{array}{c} R \cdot C : O \\ | \\ NHR'. \end{array}$$

The action of nitrous acid (or its esters) yields *isonitrosoketones :*

$$CH_3 \cdot CO \cdot CH_3 + NO_2H = H_2O + CH_3 \cdot CO \cdot CH : N \cdot OH.$$

In presence of various reagents, *e. g.*, lime, potash, sulphuric or hydrochloric acid, etc., the ketones lose water and undergo *condensation* (whilst aldehydes polymerise) : $3(CH_3)_2CO = 2H_2O + C_9H_{14}O$. Similar condensations occur between ketones and aldehydes.

The **FORMATION OF KETONES** takes place on the dry distillation of wood or of the calcium or barium salts of many organic acids or on simple heating of the latter or the anhydrides of the acids in presence of phosphorus pentoxide : $(CH_3 \cdot CO_2)_2Ca = CaCO_3 + CH_3 \cdot CO \cdot CH_3$ (*acetone*) ; if *mixed ketones* are required, a mixture of the salts of two different acids is used.[2] Noteworthy also is the formation of ketones by the oxidation of secondary

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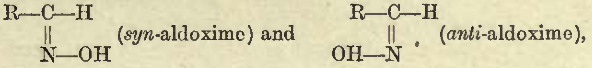
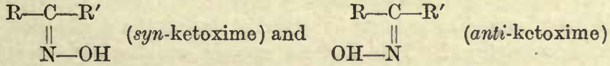
[1] For the *ketoximes* (as for the *aldoximes*) stereoisomerides exist as a consequence of the *stereoisomerism of nitrogen* (*see* p. 22) which has been studied by Beckmann, V. Meyer, Auwer, H. Goldschmidt, Hantzsch and Werner, Minunni, etc. Thus for aldoximes we have the two following stereoisomeric configurations :



$$\begin{array}{c} R{-}C{-}H \\ \| \\ N{-}OH \end{array} \text{ (\textit{syn}-aldoxime) and } \begin{array}{c} R{-}C{-}H \\ \| \\ OH{-}N \end{array} \text{ (\textit{anti}-aldoxime),}$$

whilst for ketoximes, stereoisomerides exist if the two alkyl radicals are different :



$$\begin{array}{c} R{-}C{-}R' \\ \| \\ N{-}OH \end{array} \text{ (\textit{syn}-ketoxime) and } \begin{array}{c} R{-}C{-}R' \\ \| \\ OH{-}N \end{array} \text{ (\textit{anti}-ketoxime)}$$

These isomerides are transformable one into the other, and in addition to their physical differences exhibit also chemical differences, *e. g.*, in regard to the readiness with which they lose water (aldoximes giving nitriles).

[2] This reaction may be used to demonstrate the *normal constitution* (absence of branching from the carbon chain) of acids, ketones, and hydrocarbons (paraffins), since on distilling an organic barium salt with a normal C_n chain with barium acetate, a C_{n+1} ketone is obtained which should also be normal, as the methyl group of the acetate unites with the carbonyl at the end of the chain of the acid. On oxidation, this ketone gives a C_{n-1} acid which will also be normal. From this are prepared the ketone and then a C_{n-2} acid, so that normal products are always obtained (also the corresponding hydrocarbons) by this gradual descent from a high acid of which the constitution is known to be normal.

alcohols (*see* p. 125): $CH_3 \cdot CH(OH) \cdot CH_3 + O = H_2O + CH_3 \cdot CO \cdot CH_3$. Also, with powdered metals (Sabatier and Senderens, pp. 35, 67 and 124), secondary alcohols give ketones, hydrogen being eliminated.

Ketones are also formed by the action of water in the hot on chlorinated hydrocarbons having two chlorine atoms united to the same carbon atom: $(CH_3)_2CCl_2 + H_2O = 2HCl + CH_3 \cdot CO \cdot CH_3$.

Another general method of preparing ketones is based on the interaction of zinc alkyls and acid chlorides, the additive product formed being immediately decomposed with water in such a way as to avoid the formation of tertiary alcohols: $2CH_3 \cdot CO \cdot Cl + Zn(C_2H_5)_2 = ZnCl_2 + 2CH_3 \cdot CO \cdot C_2H_5$ (*methyl ethyl ketone*).

Acetone is formed when acetic acid vapour is passed over a heated acetate or basic oxide.

ACETONE (Propanone), $CH_3 \cdot CO \cdot CH_3$, is found in small quantities in the human organism, where it is formed in larger amounts during certain diseases (diabetes, acetonuria). It is formed in considerable quantities in the dry distillation of wood and of other organic substances (calcium acetate, sugar, gum, wool-fat, etc.). It is a liquid with an ethereal odour and a characteristic burning taste, b.-pt. 56·5°,[1] sp. gr. 0·7970 at 15° and 0·7798 at 30°; it solidifies at − 95°. Its heat of evaporation is 125·3 Cals. at 56·3°; a litre of the vapour, calculated to 0° and 760 mm., weighs 2·5896 grams. It is soluble in water (from which it separates on addition of soluble salts), alcohol, ether, and chloroform; it dissolves fats, resins, ethereal oils, nitrocellulose, etc., and is readily inflammable. It dissolves only 0·26 per cent. of paraffin wax.

In aqueous solution rendered alkaline with sodium carbonate, it is oxidised with ease by potassium permanganate, and chromic acid converts it into acetic acid and carbon dioxide. With sodium it forms *sodium β-allyloxide:*

$$CH_3 \cdot C(ONa) : CH_2.$$

In the crude form, it is used in varnish, lac and colour factories and in a more or less pure state in the manufacture of iodoform. Also at the present time pure acetone is employed in large quantities for gelatinising the nitrocellulose of cordite and other smokeless powders (*see later:* Statistics), and that of celluloid so that this may be rolled. Large quantities are consumed in the manufacture of varnishes with a basis of cellulose acetate which serve as "dope" in the construction of aeroplanes. Acetone is used in making chloroform and its derivatives and in the preparation of plastic materials from casein and copal resin (which gives a kind of amber); with mannitol, arabitol or glycerine it gives camphor substitutes (Ger. Pat. 214,962). It may be used in the synthesis of indigo from orthonitrobenzaldehyde and in making isoprene for artificial rubber. It is employed to some extent to dissolve acetylene (*q. v.*) and also, in the crude state, owing to the intense burning taste it imparts, as a denaturant for spirit, from which it cannot be separated by distillation.

Industrial Preparation. Calcium acetate obtained from pyroligneous acid (*which see*) is subjected to dry distillation, the temperature being controlled so that it does not exceed 300°; the vapours evolved are rapidly cooled and condensed, giving crude acetone. In order to avoid superheating and irregularity during the distillation, moist calcium acetate is sometimes employed. The acetone vapour escaping condensation is easily recovered by passing it through towers down which a spray of sodium bisulphite solution falls; this fixes the acetone, which may be liberated by distilling the solution in presence of an alkali. In France, Buisine has utilised the wash-waters of dirty wool to prepare acetone from the

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[1] The vapour pressure of acetone vapour is 179·6 mm. of mercury at 20°, 420 mm. at 40°, 860 5 mm. at 60°, 1611 mm. at 80°, 2797 mm. at 100°, 4547 mm. at 120°, and 6974 mm. at 140°. The composition of the vapour obtained when aqueous solutions of acetone are boiled is as follows:

Percentage of acetone in solution	1	4	10	20	40	60	80	85	90	95	100
,, ,, ,, vapour .	20·4	56	81·5	87·5	92·5	94	95·3	95·7	96·3	97·5	100

fat they contain. This process has been tried on an industrial scale at Roubaix, but as yet without marked success.

During the European War acetone increased enormously in price—even to £400 per ton—and many different methods of making it were employed. In France and elsewhere it was obtained from starch by the action of special micro-organisms, which produce at the same time large proportions of butyl alcohol (now used for making various butyl esters) and higher ketones. Synthetic acetone is prepared also from acetylene, which with energetic oxidising agents (persulphuric acid, hydrogen peroxide, etc.) in presence of a mercuric salt (*e. g.*, $HgCl_2$) gives first trichloromercuriacetaldehyde, $C(HgCl)_3 \cdot OH$; the latter, with dilute HCl in the hot, yields formaldehyde and $3HgCl_2$. When passed through a tube containing a suitable catalyst at 400°, acetic acid vapour yields acetone: $2CH_3 \cdot COOH = CO_2 + H_2O + CH_3 \cdot CO \cdot CH_3$.

The crude acetone is purified by digesting it with quicklime and then distilling it from sodium hydroxide and subsequently over sodium sulphite.

STATISTICS AND PRICES. Acetone is used most largely for smokeless powder, and during the European War its consumption and price reached fantastic figures. Italy imported the following quantities of acetone, mostly from the United States:

	1910	1911	1912	1913	1914	1915	1916	1917	1918
Imports, hectolitres .	438	801	325	391	780	3,273	7,253	14,542	26,584
Value in £ . .	2,628	—	—	6,593	—	52,360	174,080	465,320	850,680

Great Britain consumed in 1908 1500 tons of acetone (£100,000), almost all imported from the United States; in 1910 1100 tons (£57,000) was imported. No certain figures regarding the enormous amounts imported during the war are available, but in 1917 the quantity probably exceeded 10,000 tons, of the value £4,000,000.

Germany imported crude acetone, especially from Austria, and exported pure acetone in the following quantities (tons):

	1907	1908	1909	1910	1911	1912
Imports .	56	87·5	271·5	482	767	912 (£38,800)
Exports .	801	357	328	414	468	1012 (£60,000)

France produces acetone to some extent and also imports it: 2015 tons in 1913, 1258 in 1914, 300 in 1915, and 357 in 1916.

Crude, impure acetone (*acetone oil*) was sold before the war at £34 per ton if dark, or £40 if pale. Acetone for industrial purposes (85 to 90 per cent.) sold at £60, the pure product (95 to 97 per cent.) at £68, and the chemically pure (98 to 100 per cent.) at £80. The bisulphite compound is also placed on the market at £40 per ton (or 14*s.* per kilo if chemically pure).

Tests for Acetone. These are of especial importance for explosive factories, where a highly purified product is required. It should dissolve in water in all proportions without rendering it turbid. When mixed with a little 0·1 per cent. permanganate solution it should retain the colour for some minutes. If acetone contains water, when mixed with an equal volume of light petroleum (boiling at 40° to 60°) two layers are formed; if no water is present, the liquids mix perfectly. At least 95 per cent. of it should distil between 56° and 56·5°, and it should not redden blue litmus paper. Krämer's quantitative iodometric test (*see* p. 129) should indicate at least 98 per cent. of acetone; Strache's method, in which phenylhydrazine is employed, may also be used.[1] The detection of acetone in other substances is effected by means of orthonitrobenzaldehyde and caustic soda, which convert acetone into indigo.

MESITYL OXIDE, $CH_3 \cdot CO \cdot CH : C(CH_3)_2$, is an aromatic liquid boiling at 132°.

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[1] *Strache's method for the indirect estimation of compounds containing carbonyl groups* (*aldehydes and ketones*). When to a solution of an aldehyde or a ketone is added an excess of a phenylhydrazine solution of definite strength, the excess of the latter which does not combine may be deduced from the amount of nitrogen liberated on decomposing (oxidising) in the hot with *Fehling's solution* [a mixture in equal volumes of the following two solutions: (*a*) 69·26 grams of air-dried copper sulphate crystals dissolved in water to 1 litre; (*b*) 346 grams of Rochelle salt dissolved in 800 c.c. of water + 105 grams sodium hydroxide, the whole made up to 1 litre with water]: $C_6H_5NH \cdot NH_2 + O = H_2O + C_6H_6 + N_2$. The test is made on 0·2 to 0·6 gram of substance (aldehyde or ketone) and the details of the operation are described in *Zeitschr. für analyt. Chemie*, 1892, p. 573, or in Hans Meyer's "Determination of Radicals in Carbon Compounds," 1899, p. 65.

PHORONE, $(CH_3)_2C:CH\cdot CO\cdot CH:CMe_2$, forms yellow, readily fusible crystals, and is obtained by saturating acetone with hydrogen chloride.

BUTANONE (Methyl ethyl ketone), $CH_3\cdot CO\cdot C_2H_5$, is a liquid, b.-pt. 81°, and is contained in wood-spirit.

KETENES

These constitute a group of substances discovered by Staudinger since 1905. Although they contain the ketonic group, CO, they differ markedly from the ketones in their great reactivity, since they are unsaturated compounds, that is, unsaturated ketones.

They are derived from the type $R_2C:CO$, which was formerly thought incapable of existing in the free state. The residues, R, may be either aromatic or aliphatic hydrocarbon radicals. All these compounds may be derived from **KETENE**, $CH_2:CO$, which is a colourless gas, b.-pt. −56°, m.-pt. −151°, and was prepared in 1908; it has a disagreeable odour (resembling somewhat those of chlorine and acetic anhydride), is poisonous and even in small quantity produces intense headache. It is easily polymerised (by metallic chlorides or tertiary bases), yielding a coloured resin. It decolorises ethereal bromine solutions instantly, and, unlike disubstituted ketenes, does not undergo oxidation in the air. The most stable and best characterised of these compounds are *dimethyl-*, $(CH_3)_2C:CO$, and *diphenyl-ketene*, $(C_6H_5)_2C:CO$; monomethyl-, $CH_3\cdot CH:CO$, and monoethyl-ketene, $C_2H_5\cdot CH:CO$, have properties similar to those of *carbon suboxide*, $O:C:C:C:O$, and resemble the isocyanates in their great reactivity. The disubstituted ketenes are coloured and readily oxidise in the air; two molecules condense with one of a base (pyridine, quinoline), and they unite with the $C:N\cdot$ group (benzylideneaniline) and with the $C:O$ group (quinones), forming β-lactams and β-lactones. All the ketenes combine with water, alcohols, or amines at the double carbon-linking, giving compounds of an acid nature. The monosubstituted ketenes are also called *aldoketenes* (colourless) and the disubstituted ones, *ketoketenes* (coloured). They are usually prepared by the action of zinc on an ethereal solution of acid halogen derivative with a second halogen in the α-position (more rarely by heating malonic anhydrides):

$$\underset{\alpha\text{-bromopropionyl bromide}}{CH_3\cdot CHBr\cdot COBr} + Zn = ZnBr_2 + CH_3\cdot CH:CO.$$

The ketenes (especially ketoketenes) are easily transformed into acids, and those that condense (the ketoketenes) with unsaturated groups (ethylene and carbonyl compounds, Schiff's bases, thioketones, nitroso- and azo-compounds) form compounds with a closed chain of four or six carbon atoms, these being resolved into two unsaturated compounds when heated. The aldoketenes undergo polymerisation more readily, giving derivatives of cyclobutane which decompose on heating.

B. DERIVATIVES OF POLYHYDRIC ALCOHOLS

The *ethers* of polyhydric alcohols are generally prepared by the methods used for ethers of the monohydric alcohols and have many properties in common with these.

ETHYL ETHER OF GLYCOL, $OH\cdot C_2H_4\cdot OC_2H_5$, boils at 127° and the **DIETHYL ETHER**, $C_2H_4(OC_2H_5)_2$, at 123°. Of the esters of glycol, the mono- and di-acetates, $C_2H_4(OC_2H_3O)_2$, which are liquids soluble in water, are well known. **Glycolchlorohydrin** or **Monochloroëthyl Alcohol**, $OH\cdot CH_2\cdot CH_2\cdot Cl$, boils at 130°, is soluble in water and is prepared by passing hydrogen chloride into hot glycol. **GLYCOLSULPHURIC ACID**, $OH\cdot C_2H_4\cdot O\cdot SO_3H$, is the sulphuric ester of glycol. **Glycol Dinitrate**, $C_2H_4(NO_3)_2$, is a yellowish liquid insoluble in water and explodes on heating; it is prepared by treating glycol with nitric-sulphuric mixture (*see later;* Nitroglycerine). It is readily hydrolysed by alkali.

ETHYLENECYANOHYDRIN, $CH_2:C:N\cdot CH_2\cdot OH$, is isomeric with **Ethylidenecyanohydrin**, $CH_3\cdot CH(OH)\cdot CN$. **Ethylene Cyanide**, $C_2H_4(CN)_2$, obtained by the action of potassium cyanide on ethylene bromide, forms a crystalline mass; on hydrolysis it gives **Succinic Acid**, $C_2H_4(COOH)_2$.

ETHYLENE OXIDE, $CH_2\cdot O\cdot CH_2$, isomeric with acetaldehyde, is a liquid with an ethereal odour, sp. gr. 0·898 (at 0°), b.-pt. 12·5°; although neutral in its reaction it precipitates certain metallic hydroxides from solutions of their salts. It is formed on distilling glycolchlorohydrin with potash. It reacts readily and dissolves in water with gradual formation of glycol.

The following compounds are also known: *Ethylene Monothiohydrate*, $C_2H_4(OH) \cdot SH$; *Glycol Mercaptan* (*Ethan-1:2-dithiol*), $C_2H_4(SH)_2$; *Dithioglycol Chloride*, $(C_2H_4Cl)_2S$, which is a very poisonous liquid. *Hydroxymethylsulphonic Acid*, $CH_2(SO_3H) \cdot OH$, is solid and is obtained from methyl alcohol and fuming sulphuric acid. *Methylenedisulphonic* (or *Methionic*) *Acid*, $CH_2(SO_3H)_2$, is formed from acetylene and fuming sulphuric acid, by way of *Acetaldehydedisulphonic Acid*, $CHO \cdot CH(SO_3H)_2$, which with lime gives formic acid and methionic acid; the latter is isomeric with ethylsulphuric acid, but cannot be hydrolysed. *Hydroxyethylsulphonic Acid*, $OH \cdot CH_2 \cdot CH_2 \cdot SO_3H$ (*Isethionic Acid*), is a crystalline mass formed by treating ethyl alcohol with sulphur trioxide; ethylene with SO_3 gives *Carbyl Sulphate*, $C_2H_4(SO_3)_2$, which forms sulphuric and isethionic acids with water.

Glycol forms also two *amines*: *Hydroxyethylamine*, $OH \cdot C_2H_4 \cdot NH_2$ (primary monovalent base, or *Hydroxyalkyl Base*, or *Hydramine*), and *Ethylenediamine*, $C_2H_4(NH_2)_2$ (primary divalent base). These may also be regarded as derived from one or two molecules of ammonia, in which all or part of the hydrogen is substituted by the hydroxyethyl group, $\cdot C_2H_4 \cdot OH$, or by ethylene, $C_2H_4<$. Thus, such compounds as the following are known: $NH_2 \cdot C_2H_4 \cdot OH$; $(NH_2)_2C_2H_4$; $NH(C_2H_4 \cdot OH)_2$, *Dihydroxydiethylamine*; $N(C_2H_4 \cdot OH)_3$, *Trihydroxytriethylamine*; $(NH)_2(C_2H_4)_2$, *Diethylenediamine*; $N_2(C_2H_4)_3$, *Triethylenediamine*; and finally quaternary bases containing alkyl groups, *e. g.*, *Choline* (or *Bilineurine*), $(CH_3)_3 \vdots N(\cdot OH) \cdot C_2H_4 \cdot OH$, or *Hydroxyethyltrimethylammonium Hydroxide*, which is obtained from trimethylamine and ethylene oxide and is found in the bile, in egg-yolk, and in the brain in the form of lecithin (*see later*); it is not poisonous, but when oxidised with nitric acid yields *Muscarine*, $CH(OH)_2 \cdot CH_2 \cdot N(CH_3)_3 \cdot OH$, which has a distinct poisonous action. On putrefaction, choline gives *neurine* (or *Trimethylvinylammonium hydroxide*), $N(CH_3)_3(C_2H_3) \cdot OH$, which is also poisonous. Many of these compounds are formed in putrefying proteins and in dead bodies, and are called *ptomaines*.

These bases are prepared by the same methods as the monovalent bases (p. 239), the primary diamines, for example, being obtained by reducing the nitriles, $C_nH_{2n}(CN)_2$, in hot alcoholic solution by means of sodium or from ethylene bromide and alcoholic ammonia at 100°. They are liquid or solid substances and have certain of the characters of ammonia. *Pentamethylenediamine* or *Cadaverine*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, boils at 179° and, being a δ-diamine, can form *Piperidine*, $C_5H_{11}N$, with separation of ammonia. *Diethylenediamine* or *Piperazine*, $C_2H_4<\substack{NH \\ NH}>C_2H_4$, melts at 104° and boils at 146°. *Tetramethylenediamine* is called also *Putrescine*.

TAURINE (Aminoethylsulphonic Acid), $NH_2 \cdot CH_2 \cdot CH_2 \cdot SO_3H$, is found in combination with cholic acid (as *Taurocholic Acid*) in the bile of various animals and also in the lungs and kidneys. It forms monoclinic prisms soluble in hot water but insoluble in alcohol, and has a neutral reaction, the basic and acid groups neutralising one another. It is not hydrolysable.

Of the derivatives of *Glycerol*, the *Chlorhydrins* or esters of hydrochloric acid are of interest; they are liquids soluble in alcohol or ether, and, to a less extent, in water. With hydrochloric acid, glycerol forms the *Monochlorhydrin*, $C_3H_5(OH)_2Cl$, of which two isomerides (α- and β-) are known, and the *Dichlorhydrin*, $C_3H_5(OH)Cl_2$, also existing in two isomeric forms. Either of these, when treated with PCl_5, gives the *trichloro*-derivative, $C_3H_5Cl_3$.[1] At the present time interest attaches also to the *formins* and *acetins*, which are used in the manufacture of non-congealing explosives.[2]

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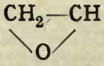
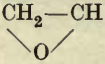
[1] According to Ger. Pat. 180,668, the monochlorhydrin is made by heating for fifteen hours in an autoclave at 120° a mixture of 100 parts of glycerol with 150 parts of hydrochloric acid (sp. gr. 1·185). The water is distilled off and the residue subjected to fractional distillation in a vacuum (15 mm. pressure); after the acid and water have been eliminated, the monochlorhydrin distils over at 130° to 150°, and the unaltered glycerine at 165° to 180°. If it is to be nitrated and used for explosives, it is sufficient to get rid of the water and acid. According to Fr. Pat. 370,224, the monochlorhydrin may also be obtained by shaking glycerine with the calculated quantity of sulphur chloride at a temperature of 40° to 50°; the water formed is distilled off in a vacuum at 60° to 70°. The *a-Monochlorhydrin*, $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot OH$, is obtained (according to Fr. Pat. 352,750) by passing hydrogen chloride into glycerine heated to 70° to 100°.

Like glycerine itself, the chlorhydrins are easily nitrated, yielding non-congealing explosives (*see later*).

[2] Monoacetin, $C_3H_5(OH)_2(O \cdot COCH_3)$, is obtained by heating for ten to fifteen hours at 100° a mixture of 10 parts of glycerol with 15 parts of 40 to 100 per cent. acetic acid, the weak acetic acid (25 to 30 per cent.) that distils over being condensed separately. Ten parts of 70 per cent.

GLYCIDE ALCOHOL,  $\underset{\diagdown O \diagup}{CH_2-CH}\cdot CH_2\cdot OH$, is a liquid, b.-pt. 162°, soluble in alcohol or ether, and also in water, with which it gives glycerol again; with hydrochloric acid it gives the chlorhydrin. It may be regarded as derived from glycerol by the removal of a molecule of water, and is prepared by the separation of HCl from the α-monochlorhydrin by means of bartya. It is isomeric with propionic acid and reduces ammoniacal silver solution. Separation of hydrogen chloride from the dichlorhydrin yields **Epichlorhydrin,**  $\underset{\diagdown O \diagup}{CH_2-CH}\cdot CH_2Cl$, which may be regarded as the hydrochloric ester of glycide alcohol. It boils at 117°, has an odour like that of chloroform and is insoluble in water. It is isomeric with propionyl chloride and monochloroacetone, and serves as a good solvent for nitrocellulose, celluloid, hard resins, organic dyestuffs, etc.

GLYCEROPHOSPHORIC ACID, $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot PO(OH)_2$, is optically active, as also are its calcium and barium salts (lævo-rotatory). It is interesting from the fact that when the hydroxyl-groups are esterified with palmitic, stearic, or oleic acid, and the phosphoric residue united to choline, it gives rise to the important group of *lecithins*, which are optically active:

$$OR\cdot CH_2\cdot CH(OR')\cdot CH_2\cdot O\cdot PO(OH)\cdot O\cdot CH_2\cdot CH_2\cdot N(CH_3)_3\cdot OH,$$

where R and R′ are fatty acid residues.

Lecithins are found in the brain, yolks of eggs, and many seeds and are soluble in alcohol, and, to a less degree, in ether; they give salts with acids and with bases and yield solid compounds with chloroplatinic acid or cadmium chloride. They are saponified by baryta, with formation of choline, fatty acids, and glycerophosphoric acid.

Of the *nitric esters* of glycerine, the most important is *trinitroglycerine* or *glyceryl trinitrate*, $C_3H_5(ONO_2)_3$, which is one of the most powerful explosives. We shall hence study it from the industrial standpoint, first discussing certain general notions concerning explosives. The manufacture of the latter constitutes one of the most interesting industries of organic chemistry, partly because of the varied mechanical appliances which it requires.

EXPLOSIVE SUBSTANCES

The name explosive substances, or explosives, is given, in general, to those solid and liquid bodies which, under the influence of heat, percussion, electrical discharge, etc., are transformed instantaneously and completely—or nearly so—into a gaseous mass with an enormously increased temperature.

If the reaction takes place in a closed space, the gases thus produced and heated exert a very considerable pressure which can be immediately transformed into mechanical work, the enclosing substance and all the surrounding objects being shattered with great violence and noise. Such a phenomenon (or effect) constitutes a so-called *explosion*, and if it attains very great rapidity and power it is termed a *detonation*. For a constant quantity of gas produced in an explosion, the effect will be the greater the higher the temperature developed in the reaction.

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acetic acid is then added and the weak acid—up to 40 per cent., which distils at 120°—collected apart. After this the temperature is raised in three hours to 250°, the weak acid still being kept separate. The crude monoacetin remaining contains about 44 per cent. of combined acetic acid and about 0·8 per cent. of the free acid. This acetin is soluble in water and serves well for the manufacture of explosive and non-congealing nitroacetins (*see* Explosives) and for gelatinising the nitrocellulose of smokeless powders (Vender, Ger. Pat. 226,422, 1906). The **diacetin** is obtained by heating glycerine with glacial acetic acid at 200° to 275°; it boils at 280°. The **triacetin,** $C_3H_5(O\cdot CO\cdot CH_3)_3$, is found in the seeds of *Eronymus europæus* and is prepared artificially from the tribromhydrin and silver acetate or industrially from the diacetin and glacial acetic acid at 250°. It boils at 268°, has the sp. gr. 1·174 at 8°, and is used as a tanning material.

THEORY OF EXPLOSIVES. The chemical reactions and physical phenomena of explosives are produced under conditions differing greatly from those in which physical and chemical properties of substances are usually studied. The pressures, temperatures, and velocities with which we have to deal in ordinary phenomena are of a very different order from that of the enormous pressures of the gases in the interior of the earth's crust, which are measured in hundreds of thousands or millions of atmospheres. So also the temperatures in various stars, *e. g.*, in the sun, reach thousands of degrees, and the velocities of the planets hundreds of kilometres per second. The phenomena now to be considered, although they do not attain these enormous magnitudes, still do approach them. Indeed, explosions give pressures of tens of thousands of atmospheres, temperatures of thousands of degrees, and velocities (of projectiles) of thousands of metres per second.

Almost all explosive substances contain oxygen (furnished by chlorates, nitrates, nitro groups, etc.), only very few, such as nitrogen chloride and iodide, and aniline fulminate, being without it. Mixtures of oxidising agents with readily combustible substances (sulphur, carbon, sugar, etc.) are explosive, but they are less powerful than those composed of single compounds which explode by themselves. This is because the elements necessary for complete combustion are in much greater proximity, being present in the molecule of the explosive itself; examples of such explosives are nitroglycerine, guncotton, mercury fulminate, picric acid, etc.

The determination of the *theoretical power* of an explosive requires a knowledge of: (*a*) the *chemical reaction* accompanying the explosion, so that the heat of the reaction, the temperature, and the volume and relative pressure of the gases formed may be deduced; (*b*) the *velocity of the reaction.* In order to understand the theory of explosives, it is indispensable to call to mind the fundamental principles of thermochemistry and of thermodynamics, for which the reader is referred to the brief account given in Vol. I., pp. 51 and 54.

(*a*) The *chemical reaction* is deduced from the difference in composition between the explosive and the products resulting from the explosion. When there is sufficient oxygen in the explosive to produce complete combustion, the nature and quantities of the gases may be calculated *a priori*, and from their heats of formation their temperature may be deduced. The total combustion of nitroglycerine, when exploded in a closed space, gives the following products (*a*): $2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O$.

When there is deficiency of oxygen, as in guncotton and other substances, it is not easy to foretell the products of the reaction, as these vary with the conditions in which the explosion occurs, and usually several reactions take place simultaneously. Further the gases found after the explosion of such products are probably not always those formed at the instant of the explosion, as at such high temperatures certain substances (H_2O, CO_2, etc.) may undergo dissociation with absorption of heat.[1]

(*b*) *The heat developed in the explosion* is deduced by calculation from the thermochemical data of the equation, but the practical result is not in accord with the theoretical calculation, since part of the heat (25 to 30 per cent.) that should theoretically be developed is transformed into mechanical work, which is what is utilised in practice. In calculating theoretically the *heat of explosion*, the *heat of formation* of the explosive (from the elements: *see* p. 25) is subtracted from the heat that should theoretically be developed in the reaction. The heat of explosion varies, however, according as it is determined at *constant volume* or at *constant pressure;* in the latter case the explosion of nitroglycerine, for example, is effected in the open air, since then the volume varies, but the pressure is only that of the atmosphere.

The heat of formation of nitroglycerine from its elements (*see* p. 25) is given by th following equation (*b*): $C_3 + H_5 + N_3 + O_9 = C_3H_5(NO_3)_3 + 98$ Cals.

The heat of reaction of nitroglycerine may be calculated from equation (*a*) given

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[1] The following Table gives the percentage compositions of the gases resulting from the normal explosion of various explosives in the calorimetric bomb:

	CO	CO_2	O_2	CH_4	H_2	N_2
Nitrocellulose powder	46·87	16·8	0·08	1·26	20·44	14·9
Gelatine dynamites	34·0	32·68	—	0·75	10·0	21·0
Carbonite	36·0	19·2	—	2·8	27·6	14·4
Picric acid	61·05	3·46	0·34	1·02	13·18	21·1
Trinitrotoluene	57·01	1·93	0·11	—	20·45	18·12

above, from which it is seen that 2 mols. or 454 grams of nitroglycerine yield $6CO_2 + 5H_2O + 3N_2 + O$. The heat of formation of $6CO_2$ is 6 × 97 = 582 Cals., and that of $5H_2O$, 5 × 68·5 = 342·5 Cals. For the nitrogen and oxygen there is no development of heat, since they are not combined, so that the total heat of reaction calculated on the gases formed in the explosion of 2 gram-mols. of nitroglycerine will be 924·5 (*i. e.*, 582 + 342·5) Cals. From this must be subtracted the heat of formation from the elements of 2 mols. of nitroglycerine, since on decomposing under these conditions of temperature the explosive first of all liberates its atoms, absorbing as much heat as is evolved in its formation from its elements (reaction *b*), *i. e.*, 196 (98 × 2) Cals. per 2 mols. The atoms thus liberated combine immediately to give the gases which result from the explosion, the heat of formation of which has already been calculated.

The true theoretical heat of explosion at constant pressure for 454 grams of nitroglycerine will hence be 728·5 (*i. e.*, 924·5 — 196) Cals., or for a kilo, 1603 Cals. The heat of reaction at constant volume—the explosion occurring in a closed vessel—is rather higher, the heat corresponding with the expansion of the gas (*see* Vol. I., pp. 27 and 52) not being absorbed, as no expansion takes place; theoretically the heat at constant volume is calculated to be 1621 Cals. per kilo.[1] Sarrau and Vieille, by direct practical measurements, found the heat of explosion of nitroglycerine at constant volume to be 1600 Cals., which confirms the accuracy of the calculation.

With substances which themselves contain insufficient oxygen for complete combustion during explosion, it is not easy to calculate theoretically the heat of explosion, since the products of the reaction are not exactly known; in such cases, various direct practical determinations must be made.

On the other hand, the presence of CO_2 alone and the absence of CO in the gaseous products of an explosion are insufficient to indicate an adequate amount of oxygen in the explosive, since in certain cases (*e. g.*, with trinitrotoluene, etc.) carbon separates during explosion. If the gases contained CO the effect of the explosion might be greater than if CO_2 were formed with simultaneous separation of inert carbon.

The *mechanical work*, in kilogram-metres, yielded by an explosive is calculated by multiplying the number of calories developed in the explosion of 1 kilo of the substance by the mechanical equivalent of heat (= 425, *see* Vol. I., pp. 51 and 52). For various explosives this mechanical work (or *potential energy*) is given in the following Table:

Nitroglycerine .	(1 kilo) = 1600	Cals. × 425	= 680,000	kilogram-metres
Explosive gelatine . .	= 1530	,,	= 650,000	,,
Dynamite . . .	= 1178	,,	= 500,000	,,
Guncotton . . .	= 1074	,,	= 456,000	,,
Fine sporting powder . .	= 849	,,	= 360,000	,,
Potassium picrate . .	= 780	,,	= 330,000	,,
Fulminate of mercury .	= 403	,,	= 170,000	,,
Nitrogen chloride . .	= 339	,,	= 144,000	,,

Owing to various causes, the total theoretical energy of explosives cannot be utilised practically; *e. g.*, the expansion of the gases at the moment the projectile leaves the cannon or gun, the friction, the heating of the barrel, etc., all constitute losses of the useful effect of the explosive.

It is not easy to calculate theoretically the *temperature of the gases* at the moment of explosion, since the specific heat of the gases at such high temperatures cannot be determined, but is certainly rather higher than the ordinary value. Further, at such temperatures dissociation phenomena occur which cannot be defined; these, however, lower the temperature, although not greatly, since with the great pressures developed the dissociation is minimal. On the other hand, with the means we possess, it is not possible to measure these temperatures directly, and only approximately can they be determined for black powder. In general, however, they are very high and in some cases exceed 4000°

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[1] For every gram-molecule of a substance passing from the solid or liquid to the gaseous state, owing to the new volume occupied, 590 small calories (Vol. I., pp. 27 and 52) are absorbed. In the explosion of 2 mols. of nitroglycerine, 14·5 mols. of gas ($6CO_2 + 5H_2O + 3N_2 + O$) are formed, and these, on expanding, will absorb 14·5 × 590 = 8550 small calories, or 8·5 Cals. per 454 grams of nitroglycerine, *i. e.*, 18 Cals. per kilo. This, added to 1603, the heat of reaction at constant pressure, gives 1621 Cals. as the heat of reaction at constant volume.

(for instance, by burning ballistite in the air, platinum with m.-pt. 1800° is easily melted), but even these temperatures, deduced indirectly, are much lower than those calculated theoretically.[1]

The *temperature of ignition* does not usually coincide with the temperature of explosion, since explosion is caused not so much by the temperature as by the pressure and other factors to be considered later; so that for explosion to occur, special conditions (detonators) are necessary. For some substances, however, *e. g.*, black powder, non-compressed guncotton, etc., the temperature of ignition, given in the following Table, is identical, or almost so, with that of explosion :

Fulminate of mercury . . .	200°
Non-compressed guncotton . .	220° to 250°
Nitroglycerine	218° (explodes at 240° to 250°)
Black powder	288°

There are thus explosives which explode when merely ignited with a match and others which are exploded indirectly by means of detonators.

The *volume of the gases* formed in the explosion may be calculated with reference to 0° and 760 mm., taking account of the fact that at the moment of explosion the water is in the state of vapour. In practice, however, it is of more importance to calculate the volume at the temperature of explosion, when a knowledge of the gases formed is possible, as is the case with nitroglycerine, and, in general, with explosives containing sufficient oxygen for their complete combustion. It is, however, not easy to calculate the volume of gas formed by products containing an insufficiency of oxygen, like guncotton, etc., with which the gases vary quantitatively and qualitatively according to the type of explosion; in such cases the volume must be determined directly.

The volume of gases is calculated (*see* Vol. I., pp. 26 *et seq.*) by means of the general formula,

$$V_t = \frac{V_o(1 + 0 \cdot 00367t)}{P},$$

where V_t is the required volume at the temperature of explosion t, V_o is the volume at 0° and 760 mm. pressure (which can be found from the weight of the gases formed), and 0·00367 is the coefficient of expansion for all gases. For such high temperatures and pressures, however, the coefficient of expansion is rather higher than that resulting from Gay-Lussac's and Boyle's laws, but this difference is compensated for by the somewhat higher specific heat of the gas at high temperatures, in consequence of which more than the theoretical quantity of heat is absorbed.

In any case, both for volume and for pressure, use may be made of van der Waals' equation (*see* Vol. I., p. 42), which was modified for the gases from explosives by Sarrau.[2]

The *pressure of the gas* is deduced from the general formula given above, V_t being

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[1] Indeed, water-vapour, formed from $H_2 + O$, should have theoretically the temperature 7927° (*see* Calculation, Vol. I., p. 465), but in the most favourable practical conditions the oxyhydrogen flame does not exceed 2500°. For carbon dioxide the heat of formation is 97,000 cals., and the specific heat 0·217, so that for 44 grams of CO_2 gas (gram-mol.) the temperature attainable would be $\frac{97{,}000}{44 \times 0{\cdot}217} = 10{,}160°$, and allowing for the fact that along with the 6 mols. of CO_2 and 5 of H_2O, the 3 mols. of N_2 and half a mol. of oxygen formed in the explosion of nitroglycerine are also to be heated the theoretical temperature of the gases from the explosion would be about 7000°. This theoretical temperature is determined in general by the formula $t = \frac{C}{ps + p's' + p''s''}$, where p, p', p'' . . . are the weights of the gases formed in the explosion, s, s', s'' . . . their specific heats, and C the total heat in calories.

[2] Clausius replaced the van der Waals equation by the following more exact expression : $p = \frac{RT}{v - a} - \frac{f(T)}{(v + \gamma)^2}$, where $f(T)$ denotes a decreasing function of the temperature T and γ is a constant. Sarrau rendered the value of $f(T)$ definite by making it equal to $K\Sigma^{-T}$, where Σ and K are two new constants. For explosion gases at a very high temperature and relatively small volume, the second term of the equation is, according to Sarrau, negligible, so that there remains $p = \frac{RT}{v - a}$.

diminished by the volume v of the mineral, non-gasifiable residue (in the case of dynamite or other mixtures), so that:

$$P = \frac{V_0(1 + 0{\cdot}00367\ t)}{V_t - v};$$

with nitroglycerine, guncotton, etc., $v = O$. P is the maximum theoretical force of an explosive, starting from its volume (solid) at the ordinary temperature, but the effect of a given explosive will be the greater as its density increases, that is, the greater the weight for the same volume; for guncotton, for example, the effect will be the greater for the same volume, the more it is compressed. Thus the relative specific gravities of different explosives are of importance, and in fact fulminate of mercury, which has a high specific gravity (five times that of ordinary powder and three times that of nitroglycerine), has a maximum rapidity of reaction and is the most powerful detonator, being capable of exerting a force of about 27,000 kilos per square centimetre (atmospheres), this being about treble that given by any other known explosive.

In practice, pressures higher than any imaginable may be attained when the volume occupied by a given weight of explosive in a closed vessel is less than the *critical volume of the gas* developed, since this critical volume (Vol. I., p. 28) cannot be diminished by any pressure, however great. If we term *charging density* the ratio between the weight of the explosive in grams and the volume in cubic centimetres occupied by it in absolutely filling its envelope (as though it were liquid or fused), this charging density corresponds with the specific gravity of the explosive; if this density equals or exceeds the *reciprocal of the limiting volume* $\left(\frac{1}{v}\right)$ into which the gases developed (critical volume) can be compressed, the pressure attained will be infinitely great and will rupture any enclosing vessel, no matter how resistant it may be. The reciprocal of the critical volume of the gases produced in the explosion is termed the *critical specific volume* (or *limiting density*), and comparison of this with the *density of charge* leads to consequences of practical importance.

	Limiting density of the gases	Specific gravity of the explosive
Black powder	2·05	1·75
Nitroglycerine	1·40	1·60
Powdered guncotton	1·16	1·20
Picric acid	1·14	1·80
Fulminate of mercury	3·18	4·42

Thus, black powder has a charging density (or specific gravity) of 1·75 to 1·82, which does not reach the limiting density, so that even if it is exploded in its own volume it does not break the envelope if the latter is strong enough to withstand the pressure developed, namely, about 29,000 kilos per square centimetre. For granular powder, the density of which is 1, the pressure is only 6000 kilos. The real density (specific gravity) of compressed guncotton is 1·2, that of nitroglycerine 1·6, and that of picric acid 1·8, all of these being superior to the limiting densities of the corresponding gases; so that when they explode in their own volume, all of these explosives burst the most resistant envelope, and, in such cases, the *velocity of the explosive wave* becomes infinitely great. Fulminate of mercury, although it has the high limiting density 3·18 (owing to the low critical volume, v), has the specific gravity 4·42 (to which the density of charge approximates) and behaves like nitroglycerine, etc.


FIG. 182.

As it is difficult to calculate *a priori* the pressures exerted by explosives, it is preferable to determine them relatively by measuring certain effects of the gases at the instant of explosion; this is done, for instance, by observing the crushing or deformation of small cylinders of copper or lead, which are termed *crushers* (Fig. 182).

The total pressure depends on the character of the explosive and on the nature of the explosion (*see later*), but more especially on the density of charge.

The *specific pressure* of an explosive is a constant (a), given by the ratio of the pressure (p) to the corresponding density of charge (d) of the explosive itself: $a = \frac{p}{d}$. This specific pressure *a* is characteristic of any explosive and *expresses the pressure developed by unit weight* (1 gram) *of an explosive in unit volume* (1 c.c.). The specific pressure is not always the maximum pressure that can be exerted, this depending, as we have seen, on the charging density in its relation to the critical volume.

Velocity of reaction or explosion. The *duration of the explosion* is of great importance, since on it depends the greater or less utility of the explosive for different purposes. The more rapid the explosion the better is the heat developed utilised, so that this may be used almost entirely in heating and expanding the gases and so increasing the pressure considerably. If, however, the reaction is slow, a large portion of the heat is dissipated by radiation and conduction.

Explosives with an extremely rapid reaction produce special effects, as they shatter the envelope or rock in immediate contact with the explosive into minute fragments—an effect often not desired. These are termed *shattering, percussive* or *high explosives* and their properties are utilised in certain cases, as, for example, where a small cavity is to be made in a rock so that a large quantity of a *progressive* or propulsive *explosive* may be subsequently introduced.

If the reaction, although rapid, is not instantaneous, the explosion produces other effects, for instance, the cleaving of large stones or rocks and the projection of fragments lying near the explosive; this progressive or rending action is the effect usually desired by miners. So also progressive explosives are used for charging guns which throw projectiles.

According as the gasification takes place more or less instantaneously (the one or the other effect may be obtained with the same substance by adding inert materials to, say, dynamite, or mixing paraffin wax with guncotton), explosives are more or less shattering. Thus, panclastite ($N_2O_4 + CS_2$) and fulminate of mercury are more shattering than guncotton, the latter more than dynamite and nitroglycerine, and this more than smokeless powder, which is a progressive explosive.

Many substances explode only with detonators (of fulminate of mercury) and the cause of the explosion in such cases is not only the high temperature produced by the explosion of the detonator, but more especially the great immediate pressure resulting from the instantaneous production of gas, this pressure and the sudden shock provoking the decomposition of the molecules of the explosive (Berthelot, Abel, Vieille). The *duration of explosion* or of gasification of the detonator is 500 times less than that of the explosive material, and the greater relative amount of heat developed in a certain time by detonators explains their greater shattering power compared with that of progressive explosives. The duration of reaction for detonators is only about $\frac{1}{1000}$ of a second, the extraordinary effect of these explosives being due to the enormous amount of energy developed (1600 Cals. for nitroglycerine) in this short time and in the small space containing them.[1]

As has been already stated, the shattering effect of a substance is rendered evident by exploding a few grams of it on a cylinder of metal (*crusher*) and the actions of different explosives are compared by means of these deformed and disfigured crushers. Fig. 183 *B* shows a leaden cylinder before the explosion, whilst *A* shows the same cylinder after 10 grams of dynamite (a progressive explosive) has been exploded on it and *C* the result of the explosion of 10 grams of panclastite (from nitrotoluene).

One and the same explosive substance may be made to give either a shattering or a

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[1] The *velocity of combustion* (or of *deflagration*) is sharply distinguished from the velocity of the explosive reaction and is made use of in certain cases, *e. g.*, in the throwing of projectiles (expansive and progressive action). The velocity of combustion of explosives depends on, and increases with increase of, the pressure at which they decompose. Another factor influencing the mode of combustion of explosives is the maximum velocity with which the pressure develops.

The *exponent of the power of the pressure*, which admits of passing from one value to the other in the increase of the pressure, is called the *modulus of progressivity*, and serves to characterise the various explosives. Thus, this modulus varies from 1·25 to 1·50 for black powders and from 1·86 to 1·87 for smokeless powders, whilst that of picric acid is 2·82 and that of *Favier's explosive* (12 per cent. of dinitronaphthalene + 88 per cent. of ammonium nitrate) 3·25. As will hence be seen, these last two explosives have the dangerous property of furnishing accidental superpressures, owing to undulatory phenomena which always accompany the combustion of substances inflammable with difficulty. In smokeless powders, the moderate progressivity compared with the great power constitutes a valuable safeguard in their use in firearms; in this they are surpassed only by black powders, which are, however, much less powerful.

progressive effect by varying the velocity of the reaction, this usually depending on the power of the *initial shock* which causes the explosion and on the physical condition of the explosive. The greater the density of the latter the less shattering it is; thus gelatinised guncotton is less shattering than the compressed cotton and this less so than the powdered cotton (*see preceding page*).

The more powerful the initial shock the greater is the amount of kinetic energy transformed into heat and hence the higher the temperature developed; therefore, also, the greater is the pressure of the resultant gases and the more rapid and powerful the effect of the explosive. The effects vary considerably with the manner in which the explosion is induced; thus, if a flame is brought near to non-compressed guncotton, the latter burns rapidly but does not explode, whilst if it is compressed and subjected to the action of a cap (detonator) of fulminate of mercury, a real and very powerful explosion occurs; similar phenomena are observed with nitroglycerine and dynamite.[1]

DETERMINATION OF THE EXPLOSION. In order to induce the explosive reaction of a substance, it is sufficient to bring it at a single point to a certain *initial decomposition temperature* (by percussion, detonation, etc.), the sharp decomposition at this point then producing a new shock which heats the neighbouring points to the decomposition temperature, and so on, the explosion being thus communicated to the whole mass by a true *explosive wave*, which is enormously more rapid than simple burning. From this will be understood the great importance of detonators, which do not serve merely for ignition; the difference will also be apparent between an ordinary explosion by ignition and percussion and that induced by fulminate of mercury detonators.

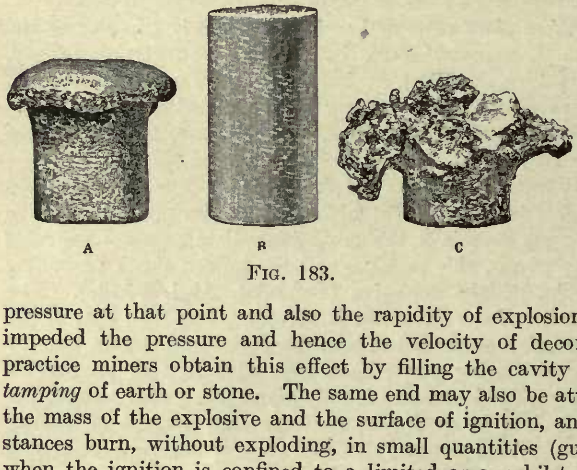

FIG. 183.

When the phenomenon of explosion is studied more closely, it becomes evident that the gases produced at the point of ignition tend to expand and hence to diminish the pressure at that point and also the rapidity of explosion, but if this initial expansion is impeded the pressure and hence the velocity of decomposition increase rapidly. In practice miners obtain this effect by filling the cavity containing the explosive with a *tamping* of earth or stone. The same end may also be attained by increasing considerably the mass of the explosive and the surface of ignition, and this explains why certain substances burn, without exploding, in small quantities (guncotton, nitroglycerine, etc.), or when the ignition is confined to a limited area, whilst a powerful explosion may occur when a large quantity of explosive is used or when it is surrounded by a source of considerable heat.

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[1] The *percussive force* (kinetic energy) of an explosive serves best to establish the *shattering power* and is calculated by C. E. Bichel by means of the formula $\frac{mv_2}{2}$, where m denotes the mass of the gases formed in the explosion, or the weight of the explosive divided by 9·81, and v is the *velocity of detonation* (*i. e.*, the time elapsing from the beginning of the explosion to its completion throughout the whole mass). For 1 kilo of an *explosive gelatine* (92 per cent. of nitroglycerine and 8 per cent. of collodion cotton) with the *charging density*, 1·63, Bichel gives a velocity of detonation of 7700 metres per second, so that the percussive force in absolute units will be: $\frac{1 \times 7700^2}{9{\cdot}81 \times 2} = 3{,}021{,}916$ kilogram-metre-seconds; *for black powder* (with a charging density 1·04) exploded under the same conditions in a closed vessel with a detonating cap, the velocity of detonation is 300 metres per second, so that $\frac{1 \times 300^2}{9{\cdot}81 \times 2} = 4587$ kilogram-metre-seconds; for *kieselguhr dynamite* (75 per cent. nitroglycerine) the velocity of detonation is 6818, and hence the percussive force, 2,369,272 kilogram-metres per second; for a *gelatine-dynamite* (63·5 per cent. nitroglycerine, 1·5 per cent. collodion cotton, 27 per cent. sodium nitrate, 8 per cent. wood meal), with a charging density of 1·67, the velocity of detonation is 7000 and the percussive force 2,497,452; for *trinitrotoluene*, with a charging density of 1·55; the velocity was 7618, and the percussive force 2,957,896; *guncotton*, with a charging density of 1·25, had a velocity of 6383, the percussive force being 2,076,589; and *picric acid*, with a charging density of 1·55, gave the velocity of detonation 8183, and the percussive force 3,412,920 kilogram-metre-seconds.

For shattering explosives (*e. g.*, fulminate of mercury) no tamping is used, since the reaction is so rapid that the atmospheric pressure, that is, the air itself with its inertia, is sufficient to maintain the pressure of the gases. Even fulminate of mercury, if ignition is effected by an electric contact (which heats a platinum wire to redness) and under an evacuated bell-jar, burns without exploding, thus confirming the tamping action of the air in the case of detonators and even of ordinary explosives; in fact, if a roll of dynamite is exploded on a bridge, the latter is cut in two owing to the tamping action of the air.

The *explosive wave* produced in the explosion of gaseous mixtures and of liquids and solids is only slightly related to waves of sound. The latter is transmitted from crest to crest with but little kinetic energy, with a small excess of pressure and with a velocity depending only on the nature of the medium in which it is propagated and of equal magnitude for vibrations of all kinds, the intensity diminishing in proportion to the square of the distance from the origin. The intensity of the explosive wave, on the contrary, remains constant, as it propagates the chemical transformation through the mass of the explosive substance, communicating from point to point of the decomposing system an enormous amount of potential energy and a great excess of pressure. The sound-wave is propagated in a mixture of hydrogen and oxygen with a velocity of 514 metres per second at 0°, but the velocity of the explosive wave or *chemical wave* in the same mixture (exploded at a point) is 2841 metres.

The velocity of propagation of the explosive wave depends on the chemical nature of the explosive, on the volume it occupies (hence on the density), and on the reaction of decomposition; the last determines the intensity of the wave and depends on the initial shock. Consequently different effects may be obtained from one and the same explosive by varying the cap (or detonator: *see later*), and if the latter is weak or insufficient the explosion is only partial or amounts to a simple deflagration, thus causing loss.

With guncotton, the velocity of this wave varies from 3800 to 5400 metres per second according to the compression or density; with nitroglycerine it is 1300, with dynamite 2700 to 3600, with explosive gelatines as much as 7700, with picric acid 6500 to 8000, with nitromannitol 7700, and with trinitrotoluene 7200 metres per second. This velocity depends only on the nature of the explosive and not on the pressure, but it varies to some extent with the nature of the envelope. For instance, in a rubber tube having a thickness of 3·5 mm. and an internal diameter of 5 mm. and covered with cloth, ethyl nitrate gives a velocity of 1616 metres, whilst in glass tubes of various diameters and thicknesses the value is 1890 to 2480 metres. The propagation of the explosive wave bears no relation to that of ordinary combustion (which is much slower). The former occurs when the inflamed gaseous molecules acquire the maximum velocity or energy of translation, *i. e.*, act with the whole of the heat developed in the chemical reaction.

Explosion by Influence. If dynamite cartridges are arranged in a long row on a flat solid at distances of 30 cm. or on a metal disc at a distance of 70 cm., explosion of the first with a fulminate cap results in the rapid and successive explosion of the remaining ones simply by influence and without the need of detonators or fuses. Air does not conduct the wave of explosive influence as well as solids, and if the cartridges are suspended in the air by wires such explosion by influence does not occur. Water conducts the explosive wave to a certain distance, but the influence gradually diminishes with increasing distance from the centre of explosion. There have been cases in which the shock of a large charge of guncotton has exploded neighbouring torpedoes; to avoid these inconveniences, so-called safety explosives are now used (*see later*), or the explosives are rendered less sensitive by gelatinising them or by mixing them with various substances, such as camphor, paraffin wax, etc.

These explosive waves are first propagated through the explosive itself, not by a single shock—which would gradually weaken as it advanced—but by a very rapid series of such shocks produced by the propagation of the explosion from point to point of the whole mass of the explosive, the kinetic energy being thus regenerated along the whole course of the wave in the exploding substance.

An explosive wave is thus distinguished from an ordinary sound-wave by the fact that the latter becomes enfeebled as it advances, whilst the former is characterised by the uniformity of the energy transmitted from point to point by a series of numerous and successive explosions throughout the exploding mass. Only the last of these explosions is transmitted with its energy to the surrounding air and to the matter on which the explosive rests, and, since it is no longer reinforced (by other shocks), it weakens as it becomes more remote. Hence explosion by influence is not due to the fact that the distant explosive transmits or propagates the explosive wave through its own mass, but is owing to the arrest and transformation, at the point of impact, of the mechanical energy—it being capable of similar (but not of all) waves—into heat energy, able to cause decomposition and explosion of the substance itself. For a long time it was thought that nitrogen iodide could be exploded by the simple note *la* struck by a musical instrument; this idea is now contested, but it is certain that some substances, on exploding, cause only the note *la* of the scale to vibrate.

The *effects* of large charges of dynamite (25 to 1000 kilos) when freely exploded are dangerous to buildings and to life for a distance of 500 metres and are felt as far away as 3 kilometres (L. Thomas, 1904).

Certain explosives decompose gradually under the action of ultra-violet rays.

CLASSIFICATION OF EXPLOSIVES. Explosives are to-day so numerous and are prepared from such different mixtures and serve such a variety of purposes that a rigorous or rational classification is difficult or impossible. Also with a large number of classes there would be many substances which might belong to more than one of them.

It will hence be preferable to limit ourselves to a description of the various explosives without any prearranged classification. They will be taken in the following order: (1) *Black powder;* (2) *Nitroglycerines and dynamites;* (3) *Nitrocellulose;* (4) *Smokeless or progressive powders;* (5) *Shattering explosives (aromatic nitro-derivatives and picrates);* (6) *Explosives of the Sprengel type;* (7) *Chlorate and perchlorate powders;* (8) *Safety explosives;* (9) *Detonating explosives and caps;* (10) *Various explosives.*

BLACK POWDER (GUNPOWDER)

This explosive, which was the first to be employed in firearms, and was the only one available for military and industrial purposes until after the middle of the nineteenth century,[1] has latterly become relatively unimportant owing to the discovery of dynamite and smokeless powders.

Ordinary black powder is a mixture of potassium nitrate, sulphur, and carbon in varying proportions according to the purpose for which it is required.[2]

For black military powders, used in guns and cannon in Italy, France, England, Russia,

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[1] It is stated, but without any real confirmation, that the Chinese knew of gunpowder as early as the first century of the Christian era, and that they used it for throwing projectiles; more certain is it that they employed mixtures of sulphur, nitre, and carbon to make rockets.

Also the ancient Indians used powders for the preparation of a kind of artificial fire. *Greek fire*, used in Greece in the seventh century, was obtained with explosive powder and probably originated in China. The Arabs were acquainted with inflammable mixtures from very remote times, whilst true gunpowder, containing sulphur, carbon, and nitre, was prepared by them only in the thirteenth century, probably after they had learnt the manufacture from the Chinese. They, however, studied its propulsive properties and constructed the first primitive guns.

In Germany it is stated that it was the monk Berthold Schwarz (a native of Freiburg, where a monument is now erected to him) who recognised the power of gunpowder in about 1310 and used it for the first time in Europe in firearms; so that the discovery, not of the powder, but of guns for throwing projectiles, is due to Schwarz. After the middle of the fourteenth century, gunpowder came into use in Germany, then in Sweden, Russia, and elsewhere for guns and cannons. Macchiavelli records that by 1386 the Genoese and Venetians had learnt from the Germans the use of powder with guns. According to Libri, cannons were made at Florence as early as 1326. The projectiles were made first of stone, then of stone covered with iron; leaden shot began to be used in 1347, and in 1388 Ulrich Beham cast the first iron shot, which became general in the fifteenth century. The mixing of the ingredients to make the powder was first carried out by hand, and it was only in 1525, in France, that powders were graded and granulated, the mixing being effected in vertical mills like those used for expressing oil from olives.

[2] After a series of experiments in Brussels in 1560, the best proportions for the ingredients were found to be: nitre, 75 per cent.; carbon, 15·62 per cent.; and sulphur, 9·38 per cent. A thirteenth-century manuscript states that the Arabs used 74 per cent. nitre, 15 per cent. carbon, and 11 per cent. sulphur. A black powder dating from 1627 and discovered in 1905 during excavation, contained 40 per cent. nitre, 24 per cent. sulphur, and 37 per cent. carbon. In 1800 Berthollet recommended as the most effective proportions: 80 per cent. of nitre, 15 per cent. of carbon, and 5 per cent. of sulphur. Berthelot has recently calculated the *theoretically* best proportions to give a maximum development of heat, his results being: 84 per cent. nitre + 8 per cent. sulphur + 8 per cent. carbon; this calculation assumes that the reagents are chemically pure, which in practice is not the case, and that the fineness and mixing of the ingredients are perfect.

China, and the United States, the maximum power is obtained without an excessive rapidity of explosion (so as not to injure the gun too much) with 75 per cent. of potassium nitrate, 15 per cent. of carbon, and 10 per cent. of sulphur, the density being increased by compressing and polishing the grains; in Germany the proportions used are 74, 16, and 10 respectively. In China until a few years ago erroneous proportions were still employed, namely, 61·5, 23, and 15·5.

The chemical reactions occurring during the explosion of black powder vary according as the explosion takes place under pressure or at the ordinary pressure (deflagration). In the first case, Abel and Nobel obtained, from 1 gram. of ordinary powder, 0·585 gram of solid products, and 0·415 gram of gas (258 c.c.), according to the following equation: $16KNO_3 + 21C + 7S = 13CO_2 + 3CO + 5K_2CO_3 + K_2SO_4 + 2K_2S_3 + 16N$; in addition there are formed traces of potassium thiocyanate and thiosulphate, and ammonium carbonate, whilst traces of sulphur and nitre remain unchanged, as the proportions taking part in the above reaction are 77·7 nitre, 10·54 sulphur, and 11·86 carbon. With 1 gram of powder exploded at the ordinary pressure, they obtained 0·769 gram of the same solid products, and 0·321 gram of gaseous products (about 193 c.c.), thus:

$$16KNO_3 + 13C + 6S = 11CO_2 + 2K_2CO_3 + 5K_2SO_4 + K_2S + 16N;$$

traces of other products are also formed, since this equation represents 82·4 per cent. nitre, 9·5 sulphur, and 8 carbon.

Sporting powder should burn more rapidly, and hence contains more nitre and a brown wood-charcoal of superior quality. In different countries the nitre varies from 75 to 78 per cent., the carbon from 12 to 15 per cent., and the sulphur from 9 to 12 per cent. Nowadays, however, most sporting powders are of the smokeless type with a nitrocellulose basis.[1] With *mining powders* the production of a large quantity of gas is required, so that the amounts of sulphur (13 to 18 per cent.) and of carbon (14 to 21 per cent.) are increased, the nitre being consequently diminished (60 to 72 per cent.); if, however, the proportion of nitre is made too small, the explosion becomes very slow, more CO is produced, and the gases are partly able to escape through the fissures produced before the end of the explosion, the useful effect being thus diminished. Hard rocks require increased rapidity of explosion, but with tufa or granite (to obtain large blocks) greater slowness of explosion is necessary.

In many countries, especially in the United States, large quantities of black mine powder with a basis of sodium nitrate are made for prompt consumption. Such powders were first patented in 1857 by the Frenchman Du Pont de Nemours (now proprietor in America of the largest explosives works in the world; during the European War 400 tons of nitrocellulose per day, besides enormous quantities of other military explosives, such as trinitrotoluene, picric acid, powder B, cordite, etc., were made at this factory); in 1910 this firm produced 45,000 tons of black sodium nitrate powder (74 per cent. nitrate, 10 per cent. sulphur, 16 per cent. wood charcoal), which is marketed in zinc cases to protect it from moisture. It is a more progressive powder than the ordinary one containing potassium nitrate.

MANUFACTURE OF POWDER. The prime materials should be prepared with great care. The *sulphur* should contain no trace of sulphuric acid, so that stick sulphur and not flowers of sulphur is used; if necessary, it is purified by distillation, and should yield less than 0·25 per cent. of residue on combustion. At the present time, use is also made of the sulphur recovered from soda residues (*see* Vol. I., pp. 206 and 596). The *potassium nitrate* is sometimes replaced by sodium nitrate, but the latter is more hygroscopic and impure. The nitre should contain less than 1 part of chlorides per 3000, and should

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[1] Smokeless *sporting powders* are of two kinds: *light*, with granules gelatinised superficially, and *condensed*, which have completely gelatinised granules and are prepared like ordinary smokeless powders (*see later*, pp. 295, 296), being often scrap from these cut to various sizes. The former or light powder is made by mixing the different components and coarsely granulating the moistened (with water or solvent or liquid ingredient) mass through sieves; these granules are rounded by subjecting them to a rotary and oscillatory movement on circular cloths moved horizontally by eccentrics, then partially drying at 50° to 60° and afterwards treating in revolving drums. The grains are finally gelatinised superficially by spraying with a solvent (*e. g.*, acetone, which gelatinises nitrocellulose, this being one of the usual components) and at the same time keeping it in motion in a vessel with a double bottom, through the jacket of which water at 50° to 60° circulates. The powder is then dried completely in a current of warm air (at 40° to 50°).

be free from perchlorates.[1] Both English nitre from India and German conversion nitre are used, after suitable purification.

The *wood charcoal* should be highly porous and should burn easily without leaving an appreciable quantity of ash;[2] in different countries, different kinds of wood are used: in Spain, flax and vine stalks; in Germany, dogwood, the alder, and the willow; in France, the poplar, lime, etc.; and in Italy, hemp stalks, etc. In some cases, charcoal from sugar, dextrin, maize, cork, etc., is used. Charcoal obtained at temperatures exceeding 430° is of no use for gunpowder.

PULVERISATION AND MIXING OF THE INGREDIENTS. In early times the ingredients were ground and mixed by hand in mortars, but machine mills were used as

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[1] For many years the superiority of English powders could not be explained, and it was attributed to the use of Indian nitre, refined in England, whilst all over Europe, *conversion* nitre, prepared in Germany, was employed. On the other hand, the Germans showed that their nitre was very pure, as it contained only 0·5 per cent. of chlorides, and they regarded the preference for English powder as the result of prejudice. In 1894, however, the elder Hellich showed that the conversion nitre contained also perchlorate and chlorate which were not shown in the estimation of the chlorides. Spontaneous explosions of powder in Servia in 1896 were ascribed by Panaotovic to the use of nitre containing perchlorates. In 1897, Kelbetz showed that the perchlorate is not distributed homogeneously through the crystals of nitre, but that some of the latter contain more (and are more explosive) and others less; hence the superiority and uniformity of powders free from perchlorate were explained. The perchlorate in nitre is estimated by Selckmann's method (1898) by fusing 5 grams of the nitre with 20 grams of pure lead in scales; the fusion is first gentle for 15 minutes until the mass becomes pasty, after which the temperature is raised for a short time. The mixture of potassium nitrite, lead oxide, and chlorides is poured into water and the chlorides estimated, the excess over the amount originally present being due to the chlorides.

[2] Under similar conditions, the readiness with which powder burns is increased by increased combustibility of the charcoal. Hence it is necessary not only to use a suitable method of preparing the charcoal, but also to make careful choice of the wood to be carbonised. Light, soft wood is preferred, and of the different parts of the plant the best are branches at least three years old (5 to 8 cm. in diameter); the bark is rejected. For powders to be used in guns, hazel or dogwood (*Rhamnus frangula*) or hemp stalks are used, whilst for cannon and mining powders, preference is given to white willow (*Salix alba*), alder, poplar, etc. *Hemp-stalk* charcoal burns the best, and about 40 parts of it are obtained from 100 of the stalks; hazel-wood gives only 33 per cent. of charcoal. The wood, freed from bark and well dried in the air for two or three years, still contains about 20 per cent. of moisture. When heated out of contact with the air, it evolves combustible gases, but the greater part of the wood blackens without burning and forms charcoal. It is of importance to determine the best conditions for carbonisation. When the temperature is not very high (280° to 340°), a light, reddish, readily combustible charcoal is obtained, whilst at higher temperatures a black, denser charcoal is obtained which burns slowly and badly, although it is a better conductor of heat and electricity.

Rapid carbonisation gives a diminished yield, but the charcoal is lighter and more friable. The charcoal is ground just before using, as in the powdered state it is much more hygroscopic and may also inflame spontaneously.

Charcoal prepared at 270° is partially soluble in caustic soda solution, whilst it is insoluble if prepared at above 330°.

Carbonisation of wood in heaps or pits is no longer employed, since the resulting charcoal is impure and non-uniform, owing to the impossibility of regulating the temperature. So that at the present time powder factories always resort to *charring by distillation*, or charring in fixed or movable *cylinders*, as proposed by the English bishop, Landloff, at the end of the eighteenth century. The distillation may be carried out in *fixed horizontal* cylinders (two to each furnace), 1·5 metre long and 0·65 metre in diameter, but with this arrangement discharging is difficult and sometimes the heated charcoal ignites. It is better to use *fixed* vertical cylinders with openings at the bottom for emptying, or movable vertical cylinders, which can be rotated from time to time during the heating. In every cylinder, a space is left for the introduction of a pyrometer to indicate the temperature of the wood. The furnace is first heated gently, and after three hours yellowish fumes, composed of water, acetic acid, methyl alcohol, etc., begin to distil. After this, the distillation continues without further heating of the cylinder. The gases are led by pipes under the hearth, where they burn at first with a bright red flame and towards the end of the distillation with a bluish red flame. When the distillation is finished, the cover of the cylinder is raised and the charcoal discharged into suitable movable drums, which are immediately closed to exclude the air. Into the cylinder, while still hot, another charge of wood is at once introduced. Each charring lasts at least ten hours. In three or four days the charcoal is cold and is then removed lump by lump from the cooling drums, any that is insufficiently burnt being rejected. The colour of the charcoal is coffee-black, the fracture being velvety and of the same colour.

An improved process of distilling wood by means of superheated steam, proposed by Violette in 1847 and improved by Gossart in 1855, was abandoned on account of its excessive cost.

In 1899, H. Güttler in Germany suggested the replacement of the superheated steam by hot carbon dioxide in order to obtain a rapid charring; after the operation, the mass may be quickly cooled by a current of cold carbon dioxide.

early as 1350. In the seventeenth century, the use of wooden stamps became widespread, but these were the cause of many explosions, so that the vertical mills again came into use, the powder being kept moistened with water during grinding. After 1754 ordinary roll mills were used. At the present time the ingredients are powdered separately, then partial mixtures of sulphur and charcoal, and charcoal and nitre, are made, these being finally united and intimately mixed. The finer the materials are powdered the better will be the resulting powder.

The charcoal and the sulphur may be powdered in the Excelsior mill (*see* p. 201, Figs. 164, 165), the product then being sieved and the coarse particles reground. The nitre is received from the refiner in the form of flour and only requires sieving.

The *binary mixtures* are prepared by placing the powdered substances in special iron drums (Fig. 184), 1·1 to 1·2 metres in diameter, and 0·6 to 1·2 metres long. On the inner periphery of the drum are 12 to 16 transverse ribs, 3 to 4 cm. thick. Hard phosphor-bronze balls, 15 to 20 mm. in diameter, are introduced with the two substances through the aperture *a*, which corresponds with the hinged cover *b*, fixed on the cylindrical wooden casing surrounding the drum. This wooden casing is connected with a leather or cloth bag, *c*, by which the mixture is finally discharged into the barrels, *d*, these being closed hermetically so as to prevent contact with the air, which might cause ignition (*see* Vol. I., Pyrophoric Substances).

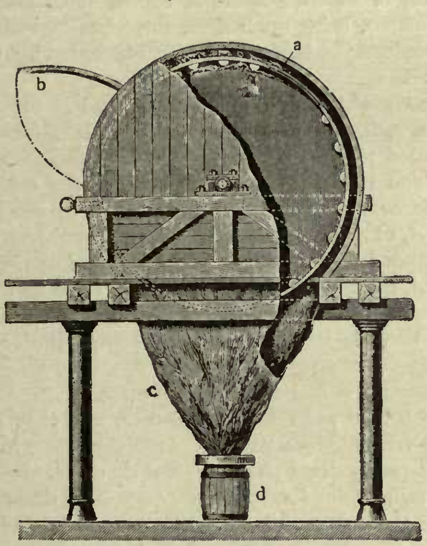

Fig. 184.

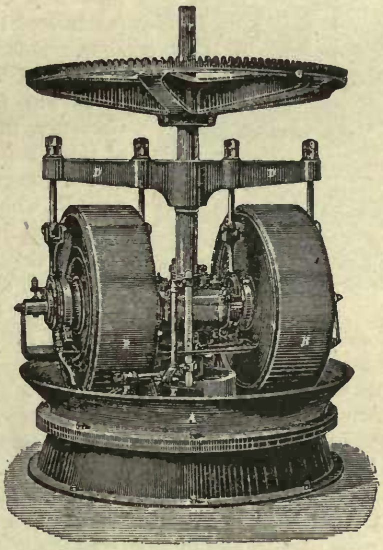

Fig. 185.

The drum is rotated about 15 to 20 times per minute for eight to ten hours, 100 to 150 kilos of the bronze balls being used per 200 kilos of the mixed substances; the balls are given a bumping motion by the peripheral ribs and so increase the fineness of the powder. When the aperture, *a*, furnished with a coarse net, is opened at the end, the powder is discharged and the balls retained for a subsequent operation (*see also* the figures of ball mills, Vol. I., pp. 651, 652).

The *ternary mixture* is prepared by mixing either binary mixture with the third constituent or the two binary mixtures (carbon + sulphur, and carbon + nitre) in the required proportions in a rotating cylinder provided with stirrers, or, better, in a drum similar to that just described. After this the mass is moistened with water and mixed, and then introduced into a stamp mill (like that shown in Vol. I., p. 653), where it is kept moistened (with about 10 per cent. of moisture) without caking. The stamps make 30 to 60 blows per minute, and their action is continued for at least twelve hours for cannon powder, eight hours for mining powder, and twenty-four hours for sporting powder. The cakes thus obtained then pass to the granulating machine.

In many factories, however, the use of stamps has been abandoned, these being replaced by vertical iron runners (Fig. 185) about 1·6 metres in diameter and 40 cm. thick, and weighing about 5000 kilos each. They rotate on a very hard iron plate 2 metres in diameter. The two runners are placed at different distances from the central shaft, which is actuated by bevel wheels above (as in the figure) or below; suitable scrapers detach the powder sticking to the runners, and others bring the powder from the edge to the centre and so under the runners. The incorporation is continued for three hours in the case of military powder and for five hours with sporting powder, the velocity of the runners being 10 to 12 revolutions per minute at first and only 1 revolution in 20 minutes towards the end of the operation, so that highly compressed cakes may be obtained. About every hour the mass is moistened with 1 to 1·5 litres of water for a charge of 20 kilos, the amount of water used depending on the hygrometric state and temperature of the air. The water dissolves the nitre, which is thus distributed uniformly and in a finely divided state throughout the whole mass.

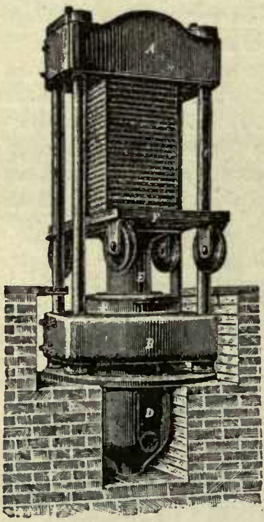

FIG. 186.

In some factories, compression of the moistened ternary mixture is effected by means of *hydraulic presses* (Fig. 186) between a number of separate layers of copper or ebonite, a pressure of 100 atmos. being applied for three-quarters of an hour. This procedure yields very compact cakes, having the density 1·7 to 1·8.

It was formerly the custom in France, and is still in Germany, to use *roller-presses* (*laminoirs*) (Fig. 187) formed of three superposed rolls; the lowest one, *C*, of cast-iron, is driven directly and transmits the movement to the middle one, *B*, which is coated with paper; this then drives the uppermost one, *A*, of chilled cast-iron. The endless band, *D*, collects the mixture falling from the hopper, *E*, and carries it between *B* and *A*, between which a pressure of 15 to 25 tons can easily be obtained by means of the lever, *L*, and weights, *P*. A knife is arranged so as to scrape the compressed powder from the band.

As a rule, moist compression gives a more uniform and also a denser mass.

After compression the cakes still contain 5 to 8 per cent. of moisture, and they are allowed to stand for seven to eight days in well-ventilated magazines. After this, those from the hydraulic presses or roller-presses are first partly dried (*see later*) and then granulated, whilst those from the stamps or incorporating mills, being less moist, are granulated directly.

GRANULATION. This operation serves the purpose of preventing the separation of the constituents, and of rendering the powder less hygroscopic and less compact (but not less dense), since the combustion of the granules is more rapid than that of the fine compact powder; also, the finer the granulation the more rapid is the combustion and the greater the mechanical effect. The finest grains are used for sporting powders, then come those for military rifles, the coarsest grains being for cannon. If sporting powder were used for military rifles, the barrel would wear out rapidly and might even split.

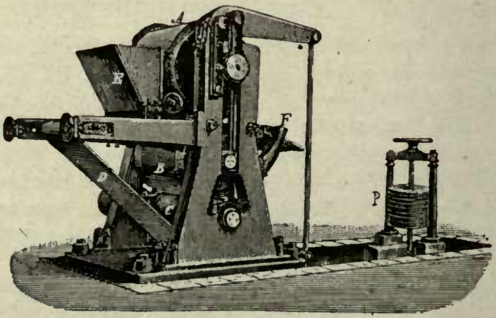

FIG. 187.

It was only after 1445 that powder for artillery was granulated, it being found that the effect was greater than that of the non-granulated and non-compressed powder. Compression with stamps or rolls came into general use in France after 1525, the compressed mass being then broken up with wooden hammers and granulated; for this purpose, the mass was spread out on a large sieve and covered with a heavy disc of wood, the sieve being then rotated and oscillated until all the powder passed through it in grains.

Later the *Lefèvre graining* machine was devised, and this is still in use in France and

Germany; this machine grades the grains into different sizes and also eliminates all dust, powders showing more regular and rapid combustion being thus obtained.

This machine (Figs. 188 and 189) is analogous to the *plane-sifter* used for flour. It consists of an octagonal board with sides, *a*, having a diameter of 2·5 metres and suspended from the ceiling by 8 ropes, *b*. This receives a circular motion by means of an eccentric formed of a vertical shaft, *c*, with an elbow-joint. This shaft is rotated at the rate of 75 revolutions per minute by the cog-wheels, *B*. On the board are fixed 8 or 10 triple sieves, *S*, to which the powder to be granulated is supplied by leather or cloth tubes, *e*. The powder falls on to the first wooden sieve, *A*, with a mesh of 3 to 4 mm., the coarse lumps being gradually broken by a disc of wood, *c*, weighing 700 grams. The grains then pass on to a second sieve, *B*, of metal, 3 to 4 cm. below, and then to the lowest one, *C*, which is of hair and retains the grains of the required size, whilst the dust falls into *D* and thence through the leather pipe, *g*, into the barrel, *p*; the uniformly grained powder is discharged into *q* through *f*.

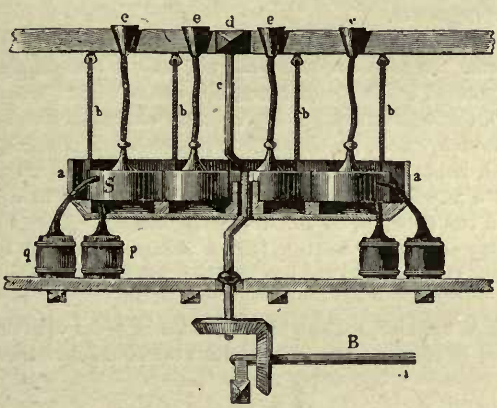

FIG. 188.

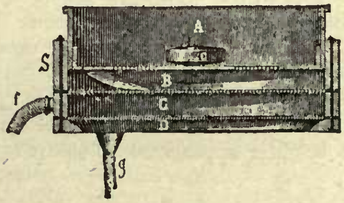

FIG. 189.

More common at the present time is the granulating machine with fluted rolls, first suggested in 1819 by the Englishman, Colonel Congreve, and subsequently improved in various ways. This machine (Fig. 190) consists of several pairs of bronze rolls, *A*, *B*, *C*, fluted longitudinally and transversely. The lumps of powder from the breaker, *D*, are raised to *E* by an endless band, and fall on to the first rolls, *A*, furnished with small pyramidal teeth projecting 10 mm., then on to the second rolls, *B*, with finer teeth (3 mm.), and finally on to the smooth rolls, *C*, which give the powder the appearance of shining scales. This distance between the rolls is adjustable, and the teeth are kept clean by means of a brush. The granulated powder falls on to a series of superposed sieves, *S*, which are oscillated at the rate of 150 vibrations per minute, and so grade the powder, the final dust being discharged at *m*. Blasting powder, which has the size of peas, is not passed through the smooth rolls. By varying the mesh of the sieves, grains of any desired magnitude are obtainable. Congreve's granulating machine gives a yield four or five times as great as that of Lefèvre (for the same consumption of power) and also forms less dust.

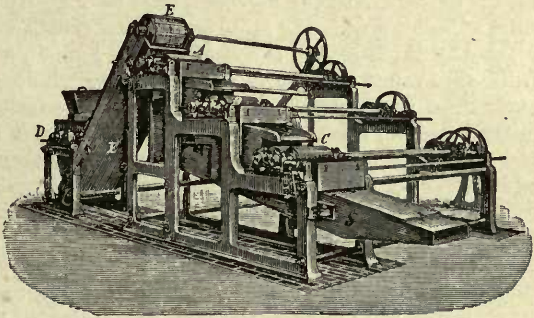

FIG. 190.

DRYING. The granulated powder is sometimes dried by spreading it out in layers 5 cm. deep on cement floors exposed to the air and sun and mixing it occasionally with rakes; this drying is continued until the moisture is reduced to 3 per cent.

The dust and residues from all the operations are mixed with the ternary mixture before compression.

Artificial drying, which is independent of climatic conditions, is however, more commonly used. In early times the powder was placed in copper pans heated directly over the fire, but this led to many explosions; later it was spread out on cloths in a chamber heated by a stove in the centre, but this also was dangerous even when the stove was outside the chamber. Nowadays drying is generally effected by air (used for the first time in England in 1780) which is heated by a network of steam-pipes and is injected into a drying-room containing the powder spread on cloth in layers 5 to 15 cm. deep, mixing with wooden rakes being resorted to about every two hours. The air passes through the powder and is carried off by flues; the drying takes 8 to 10 hours. The fire of the steam-boiler is at least 100 metres from the drying-room.

Dry powder can be powdered between the fingers, giving a pale, grey powder, but if not dry it is dark and sticks to the hands. In some factories the air used is previously dried (and is employed cold if the nitre present tends to effloresce, but hot in other cases) by being forced with a fan, *A* (Fig. 191), through fused, spongy calcium chloride or concentrated sulphuric acid contained in a leaden vessel, *D*. Thence it passes into the chest, *E*, filled with lumps of quicklime, which holds back any acid carried over. It is then heated in the brickwork chamber, *B*, by a number of pipes, *c*, supplied with steam at *d*; the warm, dry air then proceeds through the tube, *V*, to the drying-rooms.

The proposal has also been made to dry powder by heating it in a vacuum, but such a process is too costly and its efficiency low. Drying need not be complete, since the powder has still to be glazed.

GLAZING. The dried grains are rough, angular, and highly porous. In order to give a brighter appearance to the powder and to render it more uniform and dense and less hygroscopic, it is treated in wooden glazing drums (*Champy drums*, similar to those used for the binary mixtures; *see above*) after having been passed through a fine sieve to free it from adherent dust. The inner walls of the drum are first moistened and the drum slowly rotated while the powder is being introduced until about 300 kilos are present, the velocity being then raised to 12 to 14 revolutions per minute; the finer the granulation the more rapid must be the rotation. In this way the powder becomes heated to about 50° and assumes a gloss; care must, however, be taken that it does not become too hot, and towards the end of the glazing the rotation must be slackened. A little graphite is sometimes added (0·25 per cent.) to render the powder less hygroscopic and more glossy and to facilitate the rounding process. Glazing takes four to five hours for blasting powders and fifteen to twenty hours for sporting powder.

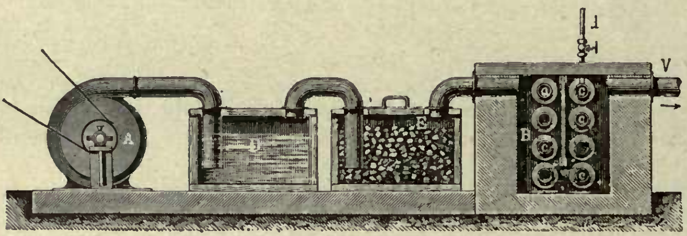

FIG. 191.

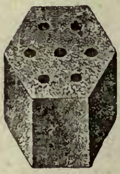

FIG. 192.

Glazing is due to the rubbing of the grains one against the other. The powder is subsequently dried completely in the usual drying-rooms, or the panels of the drum may be opened so as to allow of the escape of the warm, moist air.

Polishing and *sorting* are carried out, after the glazing and drying, to remove the last traces of dust and separate the different sizes of grains. For these purposes a battery of sieves similar to those of the Lefèvre and Congreve graining machines is used, the sieving being repeated several times. The dust contains about 75 per cent. of carbon.

PRISMATIC POWDER FOR CANNON. It was shown by San Roberto as early as 1852 that cannon give better results if charged with compressed cartridges of regular form, and the American, General Rodman, proposed in 1860 to make large grains of regular shape. The use of such powder was extended in Russia by General Doremus, and also in other countries, but was found to give better results for blasting than for military powder. In England, Armstrong's grains, in the form of hazel-nuts, met with great success and are still used. In 1879, by means of special hydraulic presses (cam-presses), Wischnegradsky prepared the first prismatic powders, six or seven holes being left in each prism (Fig. 192) to diminish the initial pressure on the cannon and give a more regular combustion. Every prism is 25 mm. high and 40 mm. in diameter, and weighs 40 grams; it has the density 1·66 and bears the mark C.66. It is used for 15 to 26 mm. guns, whilst that for larger cannon has the same volume but the sp. gr. 1·75 (marked C.75). The *brown prismatic powder* of Rottweil of Hamburg has the sp. gr. 1·86 (C.86), and is used for large cannon, since it burns slowly, gives little smoke, keeps well and imparts to the projectile a high initial velocity, which increases until the mouth of the cannon is reached; it is prepared with rye-straw charcoal and contains 78 per cent. of nitre, 3 per cent. of sulphur, and 19 per cent. of brown charcoal. The Italian *chocolate powder* contains 79 per cent. of potassium nitrate, 18 per cent. of carbon, and 3 per cent. of sulphur.

PACKING. Powder is packed in bags containing from 50 kilos, these being placed in barrels or cases coated inside with paper and outside with cloth. Each case bears a label of a colour indicating the nature of the powder (rifle, cannon, etc.). Sporting powder is placed in tin boxes holding 100, 200, 500, 1000, or 2000 grams, these being then arranged in cases containing 25 kilos.

Powder for firing volleys or ball is converted directly into cartridges, which are then stored in cases in sawdust, cotton waste, or similar packing.

CHARACTERS AND PROPERTIES OF BLACK POWDER. It has a slate-grey colour, and, if too black, either it is damp or it contains too much charcoal. Certain military powders have a brown colour, as they are prepared with reddish-brown charcoal. If rubbed on a sheet of paper it should not leave a dirty mark, as, if it does, it contains dust or moisture. When a small heap of powder is ignited on a sheet of white paper it should burn rapidly without leaving a residue or burning the paper; if very black spots remain, there is excess of charcoal, or if yellow ones, excess of sulphur. On exposure to the air, good powder absorbs only 1·5 to 2 per cent. of moisture, whilst as much as 14 per cent. may be absorbed by inferior powder. If the moisture-content of powder is only 5 per cent. it may be removed without damage to the powder, but moister powders cannot be restored to their original strength by drying, since the grains become covered with a crust of nitre. The finer the powder and the richer in charcoal, the more hygroscopic it is.

The temperatures of ignition and explosion are the same, and ignition or explosion can be produced by red-hot iron or any ignited substance, or with less ease by percussion, shock, or discharge. It is more difficult to ignite by a blow of iron on copper, or copper on copper, than by one of iron on iron or brass, or of brass on brass, etc. Powder ignites more readily by a spark or red-hot body than by a gas-flame. Guncotton burns on powder without igniting it. Different powders ignite between 270° and 320° according to the form of the granulation.

NITROGLYCERINES AND DYNAMITES

The name nitroglycerine is given improperly to nitric esters of glycerine, since they do not contain true nitro-groups (NO_2) united directly with carbon, as is often the case in benzene derivatives. On the contrary, the union is effected through an intermediate oxygen atom, so that these compounds should rather be called glyceryl nitrates.

Being a trihydric alcohol, glycerine can form three such compounds, the only one known until quite recently being trinitroglycerine, containing 18·5 per cent. of nitrogen and having very considerable industrial importance.

In 1903, Mikolajczak prepared also pure **DINITROGLYCERINE,** $C_3H_5 \cdot OH(ONO_2)_2$, containing 15·4 per cent. of nitrogen, and he proposed to use it as an explosive, as it possesses almost all the ballistic advantages of trinitroglycerine and is not easily frozen; it is, however, very hygroscopic and readily soluble in water and in acids. In 1904 he proposed to add it to trinitroglycerine to render the latter more highly resistant to frost, and since then it has been manufactured on an industrial scale at Costrop (Germany). As early as 1890 Wohl (Ger. Pat. 58,957) had already described various properties of mono- and di-nitroglycerines, including the power of lowering the freezing-point of trinitroglycerine.

In 1906 Will showed that sometimes the dinitro-compound raises, instead of lowering, the solidifying point of trinitroglycerine.

Dinitroglycerine is prepared by nitrating 100 parts of glycerine with 400 parts of nitric-sulphuric mixture containing 8 to 12 per cent. H_2O, 60 to 70 per cent. H_2SO_4, and 15 to 32 per cent. HNO_3; at the end of the reaction, the mass is poured into an equal volume of water, and the acid neutralised with calcium carbonate, when the dinitroglycerine separates as a dense, floating oil. During the reaction, the temperature is maintained at 18° to 20° by cooling with ice. Dinitroglycerine is also formed on dissolving trinitroglycerine in sulphuric acid and then diluting the solution with a little water. In whatever way it is prepared (*e.g.*, by treating 1 part of glycerine with 2 parts of sulphuric acid, separating by means of lime the glycerinedisulphuric acid formed and treating this with nitric acid, as proposed by Escales and Novak, 1906), a mixture of the two possible isomerides is always obtained: *dinitroglycerine K* (*i. e.*, $\alpha\,\gamma$-), $NO_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_3$, and *dinitroglycerine F* (*i. e.*, $\alpha\ \beta$-), $NO_3{\cdot}CH_2{\cdot}CH(NO_3){\cdot}CH_2{\cdot}OH$, which was studied by W. Will (1908). The mixture forms an almost colourless or faintly yellow oil, sp. gr. 1·47 at 15°, which freezes at below $-30°$ to a glassy mass, this distilling almost undecomposed at 146° under reduced pressure (15 mm.); at 15° it is soluble to the extent of 8 per cent. in water and at 50° to the extent of 10 per cent. In dilute sulphuric or nitric acid it dissolves in all proportions and by sulphuric acid (up to 70 per cent.) it is transformed into *mononitroglycerine* and then into glycerine. It is very hygroscopic and, when dry, dissolves or gelatinises nitrocellulose (guncotton or collodion-cotton) very well. The two isomerides may be separated by taking advantage of the fact that, in the air, the *F* compound absorbs 3 per cent. of water and is transformed into a crystalline hydrate, $3(C_3H_6O_7N_2) + H_2O$, whilst the other remains liquid. The *F*-form gives a nitrobenzoyl-derivative melting at 81°, the corresponding compound of the *K*-isomeride melting at 94°. In the dry state, the dinitroglycerines are as useful for explosives as the trinitro-compound, but when moist they are much inferior. A mixture of 50 per cent. dinitro- and 50 per cent. trinitro-glycerine freezes below $-20°$.

Of **MONONITROGLYCERINE**, $C_3H_5(OH)_2 \cdot NO_3$, the pure α- and β-isomerides are known (W. Will, 1908). These are not true explosives and dissolve to the extent of 70 per cent. in water. The α-compound melts at 58° and boils at 155° to 160° under 15 mm. pressure.

Nitrochlorhydrin, $C_3H_5Cl(NO_3)_2$, and **Tetranitrodiglycerine** (*see* p. 218) have also been proposed as *non-congealing explosives*, but better still for this purpose are the nitroacetins (V. Vender) (*see later*).[1]

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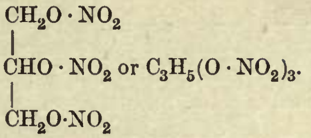
[1] **Dinitromonochlorhydrin** is obtained, according to F. Roewer (1906), by nitrating the monochlorhydrin in the same manner as glycerine is nitrated (*see later*), and is then quickly separated from the top of the nitric-sulphuric acid mixture as an oil which is easily rendered stable by washing with water and soda. It forms a faintly yellow, mobile oil of aromatic odour, sp. gr. 1·541 at 15°, soluble in alcohol, ether, acetone, or chloroform, but insoluble in water and in acids. At 180° it gives yellow vapours, and at 190° boils without detonation or deflagration, and with only slight decomposition; under a pressure of 15 mm. it distils unchanged at 121° to 123° as an almost colourless oil. It is much more stable towards pressure than nitroglycerine, although possessing almost the same explosive properties. It does not freeze even at $-30°$ and is not hygroscopic. It dissolves nitrocellulose, forming explosive gelatine, and mixes readily with nitroglycerine, giving non-congealing dynamites (with 5 to 20 per cent. of nitrochlorhydrin, Ger. Pat. 183,400), these being prepared by nitrating directly a mixture of glycerine and chlorhydrin. In order to avoid the inconvenient effects on miners of the hydrochloric acid formed in the explosion of nitrochlorhydrin, potassium nitrate is added; during the explosion this is transformed into potassium carbonate, which neutralises the acid.

Dinitroacetylglycerine, $C_3H_5(ONO_2)_2(OCOCH_3)$, is obtained by nitrating the monoacetin in the same apparatus as is used for nitroglycerine, but using an acid mixture containing a preponderance of nitric acid, *e. g.*, 65 per cent. HNO_3 and 35 per cent. H_2SO_4. The dinitroacetylglycerine, being somewhat soluble in water, is lost to some extent during the washing. It is a yellowish oil, sp. gr. 1·45 at 15°, and is soluble in alcohol, acetone, ether, nitroglycerine, or nitric acid, and almost or quite insoluble in water, benzene, or carbon disulphide. It contains 12·5 per cent. of nitrogen and with double its weight of nitroglycerine gives a mixture with 16·5 per cent. of nitrogen, which has a lower freezing-point (below $-20°$) than any other mixture of these substances. It serves well for preparing non-congealing dynamites, and as it dissolves nitrocellulose easily it may be used for gelatinising smokeless powders.

Dinitroformylglycerine, $C_3H_5(ONO_2)_2(O \cdot CHO)$, is prepared in a similar manner to the preceding compound, or, together with nitroglycerine, by nitrating the product obtained by heating two parts of glycerine with one part of oxalic acid for twenty hours at 140°. Nitroformin and nitroacetin have explosive powers rather inferior to that of nitroglycerine.

TRINITROGLYCERINE,



$$\begin{array}{l} CH_2O\cdot NO_2 \\ | \\ CHO\cdot NO_2 \text{ or } C_3H_5(O\cdot NO_2)_3. \\ | \\ CH_2O\cdot NO_2 \end{array}$$

This was discovered in February 1847 by Ascanio Sobrero,[1] who called it Pyroglycerine and established its explosive properties but regarded its industrial manufacture as too dangerous. Its chemical composition was determined by Williamson in 1854. At first it was used only in small doses as a medicine, owing to its marked power of inducing dilatation of the blood vessels, and afterwards its 1 per cent. alcoholic solution was administered in 1 gram doses under the name *glonoin*, especially by American doctors, in cases of cardiac neuralgia, nervous disorders, hemicrania, hiccough and sea-sickness. Later, after various unavailing attempts, Alfred Nobel succeeded in applying it industrially, and in 1863 established two nitroglycerine factories, one at Stockholm and the other at Lauenburg, near Hamburg; the former blew up in 1864, while the ship "European," carrying nitroglycerine, blew up in Colon harbour, and other explosions occurred in England, at Sydney, at San Francisco, etc. In spite of the large consumption of nitroglycerine in many countries, these accidents were followed by the almost universal prohibition of its manufacture. Fortunately just at this time Nobel discovered a very happy solution of the problem which completely eliminated this danger, by mixing the nitroglycerine with inert substances (*kieselguhr* or *infusorial earth*) and thus obtaining *dynamite*, this being to-day at the head of the great explosives industry.

PROPERTIES. When pure it is a dense, almost colourless or faintly yellow liquid of sp. gr. 1·6 at 15°, 1·604 at 11°, 1·588 at 25°, and when it freezes its density increases by almost one-tenth. It is odourless and has a sweetish, burning taste. It is almost insoluble in water (0·16 to 0·20 per cent. being dissolved at 15°), is not hygroscopic, and dissolves easily in concentrated alcohol, ether, benzene, chloroform, glacial acetic acid, toluene, nitrobenzene, phenol, acetone, olive oil, and concentrated sulphuric acid (sp. gr. 1·845), and to a less extent in nitric acid and still less in hydrochloric acid; it is, however, insoluble in carbon disulphide, glycerine, petroleum, vaseline, turpentine, benzine, carbon tetrachloride, and the nitric-sulphuric acid mixture used in its manufacture. In solution it will not explode. It evaporates spontaneously and in very small quantities even at 50°, and if gradually heated to 109° it begins to decompose with evolution of brown nitrous vapours.

Its specific heat is 0·356, and its heat of solidification 23 to 24 Cals.

At a red heat it evaporates without decomposing, but if it begins to boil vigorously during the heating, there is danger of explosion. According to Champion, pure nitroglycerine in small quantities boils, giving yellow vapours, at 185°, evaporates slowly at 194° and rapidly at 200°, burns quickly at 218° and detonates with difficulty at 241°, violently at 257°, feebly at 267°, and feebly with flame at 287° (being in the spheroidal state).

When heated in small quantities in the bunsen flame, it burns without exploding, and if spread in a thin layer on paper it ignites with difficulty and burns only partially. Explosion of nitroglycerine can be induced either by violent percussion at a temperature of 250°, or by energetic detonation (*e. g.*, by explosion of fulminate of mercury).

Nitroglycerine may be easily supercooled below its solidifying point. Kast (1905) showed that nitroglycerine represents a case of monotropic allotropy

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[1] Ascanio Sobrero was born at Casalmonferrato on October 12, 1812. He studied first medicine and then chemistry. In 1840 he went to complete his chemical studies in the laboratory of the celebrated Pelouze at Paris, where he stayed two years, and in 1843 he worked in Liebig's laboratory at Giessen. In 1845 he became Professor of Applied Chemistry at Turin, where he taught until 1883. He died on May 26, 1888, after a modest life, during which he filled various honorary social positions. It was always his aim that science should not be made a pretext or means of dishonourable undertakings or of business speculations.

(*see also* Vol. I., p. 208), *i. e.*, it has two freezing-points, + 2·1° and + 13·5°, corresponding with different crystalline forms.[1]

The heat of transformation of 1 gram of liquid nitroglycerine into the solid labile form is 5·2 cals., and that of the latter into the solid stable isomeride 28 cals., this being obtained by seeding with a crystal of the stable form and stirring at 0° (Hibbert and Fuller, 1913).

When frozen, nitroglycerine explodes with more difficulty than in the liquid form. Pure nitroglycerine will not redden blue litmus paper or turn starch paste and potassium iodide blue, unless it contains free acids or nitrous compounds due to partial decomposition.

Impure nitroglycerine readily decomposes and may explode spontaneously, whilst in the pure state it keeps indefinitely. A sample of nitroglycerine (200 grams) prepared by Sobrero in 1847 is still kept under water in the Nobel factory at Avigliana.

When decomposing, nitroglycerine turns green, owing to the formation of N_2O and N_2O_3; CO_2, CO, H_2O, N, and O (*see also* p. 259) are also successively formed. In exploding, 1 litre of nitroglycerine produces 1298 litres of gas, which, at the temperature of explosion, occupies a space of 10,400 litres.

In large doses nitroglycerine is poisonous and its vapour causes headache (especially at the back of the head), giddiness, and vomiting. These effects are produced even by working with or simply touching nitroglycerine, and are cured by means of cold compresses on the head, by breathing fresh, pure air, and by drinking coffee and taking suitable doses of morphine acetate.

Workmen who handle the nitroglycerine paste during the manufacture of the various dynamites become habituated to it in two or three days and afterwards feel no ill effects. Nitroglycerine is moderately easily decomposed by alcoholic potassium hydroxide (with separation of glycerine), and, when necessary, this reaction is employed to destroy and render harmless small quantities of nitroglycerine; similarly benches or floors on which nitroglycerine is spilt are washed with caustic alkali solutions:

$$C_3H_5(ONO_2)_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3\cdot COOK + H\cdot COOK + 3H_2O;$$

a little ammonia is also formed. With reducing agents it gives ammonia and glycerine, whilst with concentrated sulphuric acid it yields nitric acid and glycerinesulphuric acid.[2]

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[1] Both nitroglycerine and also dynamites and smokeless powders prepared from it are liable to solidify, and although they are then more stable (or as stable as the liquid, as was shown by Hess, Dupré, Cronquist, Will, etc.) the thawing is accompanied by danger, and when not carried out with great precautions has often led to fatal explosions, these being sometimes caused by the mere rubbing of the crystals. Indications will be given later of the precautions taken in magazines to prevent freezing, and mention may be made here of the attempts which have been made to render *nitroglycerine non-congealable.* As early as 1895 it was proposed to add nitrobenzene to nitroglycerine to lower the freezing-point, and later the use of orthonitrotoluene was suggested, but the practical results were not very satisfactory in either case, the depression of the freezing-point being very small. Substances were required which were almost as explosive as trinitroglycerine, and were insoluble in water and stable on heating, and, in addition, were good solvents for nitrocelluloses (for making smokeless powders). These conditions were well satisfied by the *nitroformins* and *nitroacetins* tested by Nobel as early as 1875, but rendered practically useful in 1906 by V. Vender. The best results are given by *dinitromonoacetin*, which is obtained from the *monoacetin* of glycerine prepared by the ordinary method used for esterifying alcohols with acids (*see later:* Esters). Forty parts of the monoacetin are introduced slowly into a mixture of 100 parts of nitric acid (sp. gr. 1·530) and 25 parts of oleum or Nordhausen sulphuric acid (containing 25 per cent. of free SO_3), the mass being cooled so that the temperature does not exceed 25°. The whole is then poured into water and washed with cold and afterwards with hot (70°) dilute soda. By this means an oil is obtained having sp. gr. 1·45 and containing 12·5 per cent. of nitrogen; it is insoluble in water, carbon disulphide or benzine, but dissolves unchanged in nitric acid, nitroglycerine, methyl or ethyl alcohol, acetone, acetins, etc. Even in the cold, it has considerable solvent and gelatinising power for collodion-cotton and guncotton (with 13·4 per cent. of nitrogen) and the resulting explosive gelatines do not freeze even at − 20°. Naukhoff (1908) has proposed the addition of nitromethane or nitroethane to dynamite to lower its freezing-point; mono- and di-nitroglycerines also give good results (*see* pp. 273, 274). In 1866, Rudberg patented in Sweden the addition of nitrobenzene to obtain non-congealing dynamites. In the Arendonck factory (Belgium) Leroux in 1903 successfully used liquid dinitrotoluene to render dynamite incongealable; Mikolajczak in 1904 utilised dinitroglycerine for the same purpose. The number of accidents has been reduced to one-half in this way.

[2] In certain practical cases the following reactions may be of interest: Nitroglycerine is not altered by prolonged contact with nitrates of Ca, Co, Na, Ba and K, with chlorides of Ca, Ba

Characteristic Reactions. According to Weber, small quantities of nitroglycerine are detected by treatment with aniline and concentrated sulphuric acid; a reddish-purple coloration is obtained which turns green on addition of water. To establish the *purity* and keeping qualities of nitroglycerine, the nitrogen is determined and Abel's heat test carried out (*see later*, Testing of Explosives); if it is satisfactory, 2 c.c. of it withstands 15 to 25 minutes' heating at 82° without giving sufficient nitrous vapours to be detectable by means of starch and potassium iodide paper.

This reaction is, however, given by nitroglycerine kept for a few days at a temperature exceeding 45°, or for a long time below this temperature.

PREPARATION. It is obtained by the action of a mixture of nitric and sulphuric acids on glycerine :

$$C_3H_5(OH)_3 + 3HNO_3 = 3H_2O + C_3H_5(NO_3)_3.$$

The mono- and dinitro-compounds are probably formed as intermediate products of this reaction.

The presence of sulphuric acid, which plays no apparent part in the change, is usually regarded as being necessary to maintain the nitric acid at a high concentration, *i. e.*, to decompose the hydrates formed by nitric acid with the water from the reaction (HNO_3, H_2O—HNO_3, $3H_2O$) and so regenerate monohydrated nitric acid, which acts on the glycerine (Kullgren, 1908). If the function of the sulphuric acid were merely to fix the water, phosphoric acid could be used in its place, but if this is done no nitroglycerine is obtained (*see* succeeding Note).

The excess of the nitric-sulphuric mixture which is always used helps to produce a moderately complete separation of the nitroglycerine, which has a slightly lower density, so that it is possible to recover the acids employed. Although nitroglycerine is soluble in sulphuric or nitric acid alone, it does not dissolve in the mixed acids, but if one of the two acids is in large excess, a considerable amount of nitroglycerine remains in solution and is lost. In the nitration, the whole of the glycerine cannot be added at one time, since sufficient heat would in that way be developed to produce decomposition and explosion of the nitroglycerine instantaneously formed. It is also not convenient to reverse the operation, that is, to add the mixed acids gradually to the glycerine, the greater density of the latter rendering rapid and homogeneous mixing difficult ; it is hence preferable to run the glycerine slowly into the acid mixture and to keep the latter continually and thoroughly stirred and cooled.

MANUFACTURE. The theoretical proportions of the reacting substances [1] would be 100 parts by weight of glycerine and 205·43 of pure nitric acid, the theoretical yield of trinitroglycerine being then 246·74 parts. On a large scale, however, the whole of the nitric acid does not come into immediate contact with the whole of the glycerine, and it is hence better to use a slight excess of nitric acid (240 parts or even more); the amount

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and Fe, with sulphates of K, Na and Ca, or with calcium carbonate. With silver nitrate it gives a black precipitate of silver oxide, while with stannous chloride it precipitates tin peroxide and forms a mirror at the surface. It reduces potassium dichromate partly to chromate, and gives a slight precipitate of copper oxide with copper sulphate and a voluminous precipitate and nitrous vapours with ferrous sulphate. Sulphides, including hydrogen sulphide, decompose nitroglycerine slowly with separation of sulphur and glycerine.

[1] The prime materials used in the manufacture of trinitroglycerine should be subjected to rigorous control; the *glycerine* should be pure and distilled and should satisfy the requirements indicated on p. 222. The *nitric acid* should have a specific gravity of 1·500 (48° Bé. or about 95 per cent. HNO_3) and should not contain more than 1 per cent. of nitrous acid (the final mixture less than 0·3 per cent.), *i. e.*, it should not be yellow, as otherwise an increased amount of heat is evolved during nitration and the yield is lowered. The *sulphuric acid* should be pure, with a sp. gr. of 1·8405 (*i. e.*, at least 96 per cent. H_2SO_4) and acid containing more than 0·1 per cent. of arsenic should be avoided; lead and iron should also be absent as they might lead to reduction. When nitrations are carried out with nitric-sulphuric acids almost free from water (1 to 2 per cent.) the sulphuric acid is replaced by *oleum* or Nordhausen acid (*see* Vol. I., p. 317), *i. e.*, acid containing 20 per cent. or more of dissolved sulphur trioxide.

According to Markovnikov (1899) the sulphuric acid first forms the intermediate product, $OH \cdot SO_2 \cdot ONO_2$, with the nitric acid.

of sulphuric acid employed always exceeds that of the nitric acid (about 1½ times). In modern factories the following proportions are often used: 100 kilos of glycerine, 240 to 270 kilos of nitric acid (96 per cent.), and 330 to 360 kilos of sulphuric acid (96 per cent., partly oleum).

In the best factories the *practical yield* was formerly 200 to 210 kilos of nitroglycerine per 100 of glycerine. In 1900, however, the French works began to make use of highly concentrated acid mixtures (the 5 to 6 per cent. of water being diminished to 2 to 3 per cent. by mixing oleum in place of sulphuric acid of 66° Bé. with the concentrated nitric acid). Later Nathan and Rintoul employed mixtures containing only 1 to 1·5 per cent. of water, the yields rising to 225 to 228 per cent. Yields of 232 per cent. were then obtained by means of water-free mixtures, from which the nitroglycerine separates better owing to its less solubility and to the greater difference in density. The yield may be improved still further and the duration of the nitration reduced to one-half by cooling the acid mixture during the reaction by means of brine from a refrigerating machine, the temperature being thus maintained at about 10°.

The highest yields appear to be obtained with a mixture containing 46 per cent. of HNO_3 and 54 per cent. of H_2SO_4 (Hofcoimmer, 1912).

The low value of the practical compared with the *theoretical yield* (246·7) is due to the fact that towards the end of the reaction there is very little free nitric acid and the last portions of glycerine added are nitrated only with difficulty, and hence remain dissolved in the sulphuric acid.

The mixture of nitric and sulphuric acids, which is prepared separately, is made by pouring the sulphuric acid slowly into the nitric acid (not *vice versa*) in an iron vessel, the mixture being kept well cooled and stirred. With this procedure there is no danger of the acid spurting, and no production of nitrous fumes, since the development of heat is gradual. This mixture is forced by means of elevators (*Montejus*) or pulsometers working with compressed air (Vol. I., p. 302) into tanks which feed the leaden apparatus in which the glycerine is nitrated.

During recent years, many vitriol and explosives works have made considerable use of Kuhlmann emulsors (or *Mammoth pumps*) for raising concentrated acids, which are rendered lighter by emulsification with air (*see illustration*, Vol. I., p. 304).

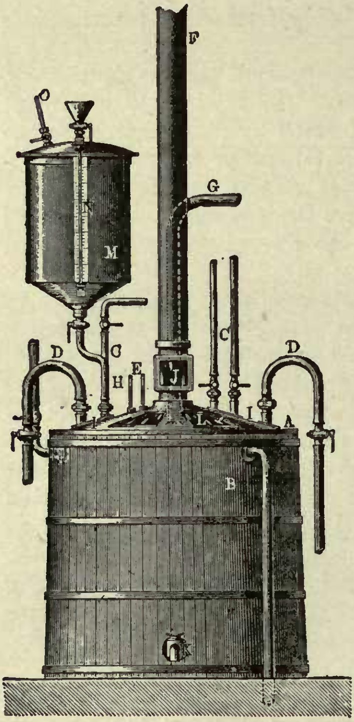

Fig. 193.

The leaden nitration apparatus is shown in Fig. 193. It is surrounded by a wooden jacket inside which water circulates. Inside the vessel are peripheral leaden coils through which large quantities of cold water are continually passed by means of the two tubes *D*. The tubes *C* lead dry compressed air to the bottom of the liquid, which is thus kept thoroughly mixed. The tube *F* serves as exit for the air, and for any nitrous vapours which may be evolved and may be observed through the window, *I*; these vapours are recovered in small condensation towers sprinkled with a little water. The cold acid mixture is first introduced through the pipe *G*. The glycerine, at a temperature of 20° to 25° (if colder it would be too viscous), is measured in the reservoir, *M*, and is passed, by means of compressed air supplied through *O*, slowly into the tube *H*, and thence into a perforated circular pipe at the bottom of the apparatus. Two thermometers, *E*, show the temperature of the reacting mass at any moment.

The bottom of the apparatus is slightly inclined and at the lowest part is inserted a large stoneware tap, *K*, with an ebonite screw containing an aperture of at least 5 cm. It is convenient to have two of these taps so that, in case of danger, the whole of the mass may be rapidly discharged into a vessel of water underneath (*drowning* of the nitroglycerine). In such an apparatus, the same quantity of nitroglycerine is produced each time and the treatment of 100 kilos of glycerine requires less than half an hour.[1] In America as much as 2000 kilos of glycerine are worked at one time in open vessels provided with stirrers, but the risk, in case of explosion, is greatly increased. At the conclusion of the operation the nitroglycerine (sp. gr. 1·6) floats on the acids (sp. gr. 1·7) and is separated by means of a suitable decanting apparatus (Fig. 194) to the bottom of which the whole mass is passed through the tube *K*. The apparatus consists of a leaden tank with its base sloping towards the centre and supported by a wooden structure; the cover, *C*, is raised on wooden joists, *B*. The tube *D*, with the glass window, *E*, serves to carry off any gas which may be evolved; a thermometer is inserted into the vessel at *t*. The tube shown at the bottom and in the centre of the apparatus communicates with two or three taps, *H*, and is also fitted with a window, *F*.

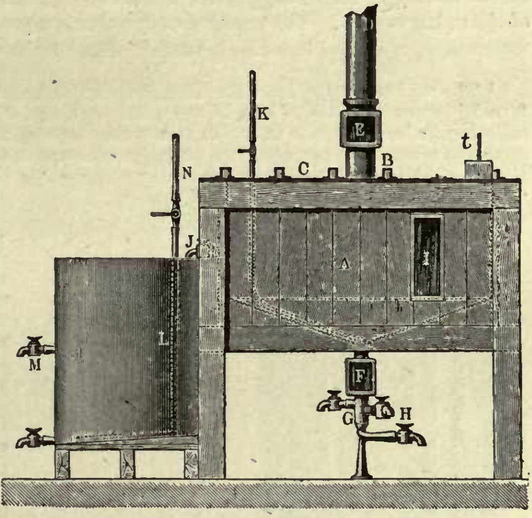

Fig. 194.

After half an hour, the nitroglycerine in this vessel separates into a distinct layer, as may be seen through *I*. The surface of separation of the two layers coincides very nearly with the tap *J*, so that the nitroglycerine may be discharged almost completely through the tube *J* into the lead-lined wooden tank, *L*.[2] The acid that remains is discharged through one of the taps, *H*, it being noted

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[1] Before the reaction is started the acid mixture in the apparatus is cooled to 15° to 18°, a stream of air (as dry as possible) being passed through it and cold water being circulated through the coils. If brine from an ice machine is used, the temperature may be lowered to 8° to 10°.

The temperature during the reaction should not exceed 25° to 30° (18° to 20° if brine is used), and it may be regulated by passing the cooling water more or less rapidly through the coils, and, if necessary, through the wooden jacket; increase of the air-current also helps to lower the temperature. Rise of temperature and consequent explosion were at one time due principally to the use of impure glycerine, but nowadays are generally due to slight escape of water from the coils. In order to avoid such danger, the apparatus and coils are tested at least once a day, usually in the evening, when the plant is free; water under pressure is forced into the coils and jacket and left until the morning, when any leak can be detected. Although the apparatus is constructed of very thick plates, the lead corrodes in time; tests made with aluminium apparatus (proposed by Güttler) have not been very successful. Some works now employ more solid vessels of wrought- or cast-iron, which are more easily cooled.

Boutmy and Faucher (1872) avoid the dangers of violent reactions by first dissolving, *e. g.*, 100 parts of glycerine in 320 of sulphuric acid and then pouring the solution into a mixture of 280 parts of nitric and 280 of sulphuric acid. After twelve hours the reaction is complete, the yield being 190 per cent., calculated on the weight of the glycerine taken. This method did not give good results in England, but has been applied in France. The procedure is, however, irrational, since the operation occupies twelve hours, the duration of the contact of the acid with the nitroglycerine and hence the danger period being prolonged. A factory using this method did, indeed, blow up and the process was then abandoned.

Kurtz (Ger. Pats. 6208 and 8493) increases the yield and accelerates the reaction by emulsifying the glycerine with air and passing it under the acid mixture, a more intimate mixture being thus obtained. R. Evers (Ger. Pat. 183,183, 1902), instead of mixing with a current of air, which always carries off a little acid, passes the acid mixture and glycerine at the same time through a pulveriser into the apparatus.

[2] Not infrequently, owing to the formation of a colloidal froth of silicic acid, the nitroglycerine separates very slowly from the acids, two or three hours being sometimes required for a good separation and the danger of decomposition thus increased. Various investigations have been made with a view to discover a means of preventing such slow separation, which is often due to the use of glycerine of poor quality or of impure acids. Good results have been obtained by the addition, before the mass is discharged into the separator, of a small quantity of sodium fluosilicate, the bubbles of hydrofluosilicic acid thus developed causing rapid separation of the nitroglycerine. Reese (Brit. Pat. 20,310, 1905) adds at the beginning of the reaction, about 0·002 per cent. of sodium fluoride, calculated on the weight of the glycerine. According to Ger. Pat. 249,579 of 1911, 0·02 to 0·05 per cent. of finely powdered talc or kaolin (on the weight of the glycerine) may be added to the acid before the reaction is started.

through *F* when a turbid layer appears, as this separates the acid from the nitroglycerine and contains various nitro-products and certain impurities.[1]

The tap, *H*, is then closed and this liquid is passed through other taps into suitable washing and decanting vessels (*see later*). The nitroglycerine in *L* is washed with water and is then agitated by passing compressed air through the perforated pipe, *N*, for about fifteen minutes; the nitroglycerine is allowed to settle and the water decanted off by means of the upper tap, *M*. The washing with water is repeated two or three times, all the washing water being collected in a single tank.[2] Finally the nitroglycerine is passed into a similar

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[1] The acid separated from the nitroglycerine and containing about 70 to 73 per cent. H_2SO_4, 9 to 10 per cent. HNO_3, 15 to 16 per cent. H_2O, and 3 per cent. of dissolved nitroglycerine, is collected in leaden tanks in which it remains for one or two days, during which time a small quantity (about 0·5 per cent.) of nitroglycerine separates at the surface. The dangers of this *slow separation* are sometimes avoided by neglecting the nitroglycerine which separates after four to five hours; to avoid danger in succeeding nitrating operations, a large proportion of the nitroglycerine remaining dissolved is decomposed by adding cautiously 4 to 5 per cent. of water, so as to raise the temperature to 35° to 40° and then again mixing the mass by means of air (part of the trinitroglycerine is thus transformed into soluble dinitroglycerine). These recovered acids, which are utilised again, are first denitrated in the apparatus shown in Fig. 195. This consists of a tower *A*, 4 to 5 metres high, composed of six or seven rings of volvic stone in one piece, fitted by means of grooves and luted with powdered asbestos and a little sodium silicate. The inner and outer diameters are respectively 30 to 40 cm. and 50 to 65 cm. These rings are surrounded by tightly fitting cast-iron hoops. The internal space is filled with fragments of silica (quartz), glass or stoneware, resting on a grid of volvic stone or earthenware. The acid to be denitrated passes from the tank *D* down the tower as a spray, while a current of steam, superheated to about 350° and mixed with a little hot air (at 400°) is passed in at the bottom through the cock *a*. The acid feed is regulated so that sulphuric acid at about 150° collects at the base of the tower, while the nitric acid vapour issuing through the tube *C* has the temperature 110° to 120°. By introducing this hot mixture into the tower, steam is economised and the nitric acid condensing in the stoneware pipes *G* is rendered more concentrated (usually 60 to 65 per cent., although with care 85 per cent. may be reached) and, if sufficient air is used, contains little nitrous acid (3 to 5 per cent.). The gases not condensed in the pipes *G* are completely condensed in the ordinary stoneware towers fed with a little water or dilute nitric acid (*see* Vol. I., p. 388), being passed from one tower to the other until acid of 32° to 36° Bé is obtained.

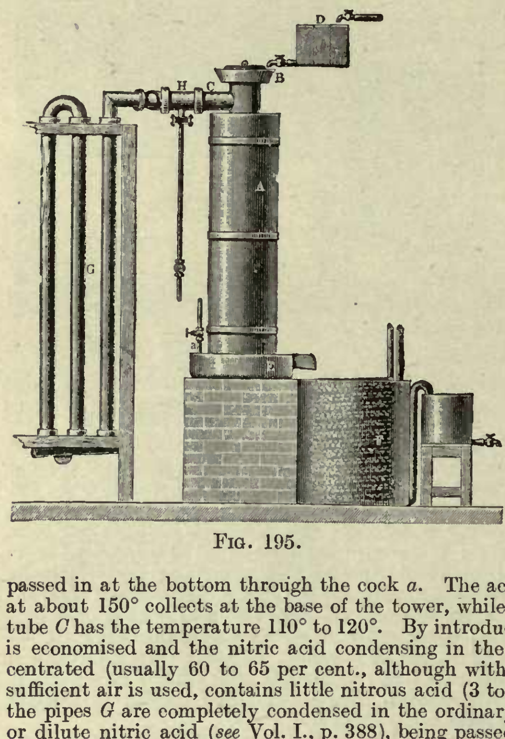

Fig. 195.

The sulphuric acid at last reaches the bottom of the tower, *A*, where it collects in the basin, *E*, and thence passes through the leaden cooling coil, *F*. The acid thus obtained is darkened by the impurities present and has a density of about 56° to 58° Bé; it is usually concentrated in the Kessler apparatus or in Gaillard towers (*see* Vol. I., p. 308).

During recent years, instead of the sulphuric and nitric acids being recovered and concentrated separately, it has been found preferable to send the acid mixture—after decomposition of the dissolved nitroglycerine (*see above*)—directly but carefully into the vessels (already containing the sodium nitrate) in which nitric acid is made. Some prefer to *revivify* the acid mixture, *i. e.*, to bring it up to its original strength by adding the necessary quantities of fuming nitric and sulphuric acids, so that it may be used again for the production of fresh quantities of nitroglycerine; for this purpose, sulphuric anhydride or oleum is added slowly to the required amount of concentrated nitric acid and the mixture then poured into the weak acid. For this process of recovering the weak acids (by which the 2·5 per cent. or so of nitroglycerine dissolved in the acid is recovered) to be employed, a cheap supply of sulphuric anhydride or oleum must be available (oleum at less than 40*s*. per ton).

[2] The *wash-waters* from all the preceding operations are collected in an inclined lead-lined tank called the labyrinth, which is divided into a number of chambers by vertical leaden walls perforated alternately at the top and bottom. The wash-waters enter slowly at one end of the tank and traverse a long up-and-down course, gradually depositing the emulsified or suspended drops of nitroglycerine before the opposite end of the tank is reached. The nitroglycerine collected at the bottom is discharged through suitable taps and added to that in the washing apparatus.

vat where it is *stabilised, i. e.*, washed alternately with very dilute soda solution and water until the wash-water no longer has an acid reaction towards litmus and the nitroglycerine has a feeble alkaline reaction (0·01 of alkalinity, which disappears later).

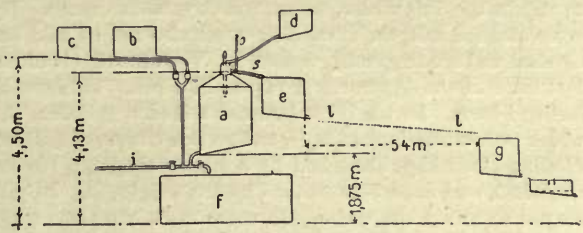

FIG. 196.

In the British Government factory at Waltham Abbey, Nathan, Thomson, and Rintoul (Brit. Pats. 15,983, 1901; and 3020, 1903) prepare nitroglycerine in large leaden vessels (*a*, Fig. 196) with inclined bottoms; 300 to 500 kilos of glycerine are allowed to run into an anhydrous acid mixture in the proportion of 267 kilos of H_2SO_4 and 243 kilos of HNO_3 per 100 kilos of glycerine, and at the end of the operation, after 50 to 60 minutes' rest, the acid recovered from a preceding operation is passed from the tank, *c*, to the bottom of *a*. In this way the nitroglycerine is displaced and caused to discharge through *s* into the washing vessel, *e*, exit for the vapours being supplied by the tube *o*. When all the nitroglycerine has been forced out, a little of the acid mixture is drawn off by the pipe *i*, 2 to 3 per cent. of water being then slowly added to the remainder, which is mixed meanwhile with a current of air. By this means the dissolved nitroglycerine is decomposed and the dangers of slow separation in any of the vessels avoided (*see* preceding Note). The acid is immediately denitrated, after sufficient has been passed into the tank, *c*, to displace the nitroglycerine of the succeeding operation. *b* is the tank in which fresh acid is mixed, *f* the vessel for drowning, *g* that for stabilising, and *h* the filter for the nitroglycerine, these two being at a considerable distance from *e*, so that the nitroglycerine may be conducted to them as soon as it has undergone its initial rough washing. The nitrating apparatus is shown in section in Fig. 197. Yields of as much as 230 per cent. are obtained with this Nathan-Thomson process, which is now used in all countries.

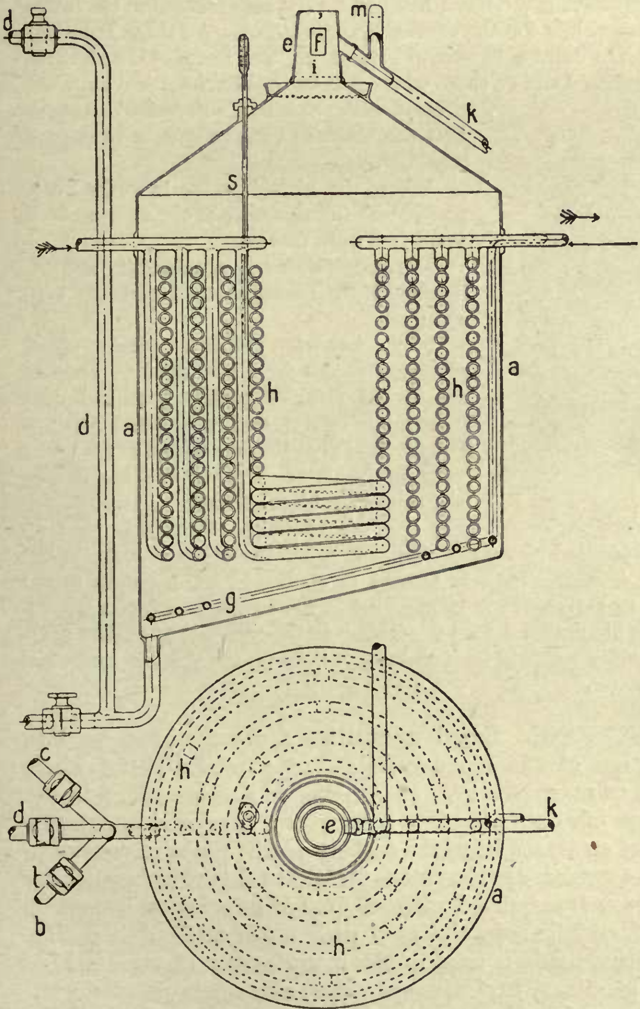

FIG. 197.

FILTRATION. The washed nitroglycerine is carried in hardened rubber or ebonite buckets to the filters, which are merely wooden frames covered with woollen cloth or felt to retain the impurities, scum, gummy matters, etc. By covering these cloths with a layer of dried salt, the emulsified water also can be held back. The cloths rapidly become blocked and are frequently renewed. The filtration is often, especially in England, effected by means of the apparatus shown in Fig. 198. This consists of a lead-lined tank, *A*, with inclined base. In the lid is inserted a leaden cylinder, *G*, with a metal gauze bottom on which rests a filtering cloth, *N*, and on this a layer of sodium chloride, *O*, covered by another filtering cloth kept stretched by a leaden ring, *Q*; the free part of this cloth is folded, stretched, and fixed by a conical leaden weight, *R*. In place of salt, a sponge may be employed to retain the water. In some cases complete separation of the water from nitroglycerine is obtained by leaving the latter at rest for a couple of days in a tepid place (30°) and then decanting it, but there is then some risk, owing to the prolonged accumulation of large quantities of nitroglycerine.

In the working of nitroglycerine, each operation is usually carried out in a separate building, that in which the explosive is produced being at a very high elevation, the nitroglycerine then flowing to lower points for the succeeding operations. All these buildings are of wood so as to diminish the damage in case of explosion. The floors of the sheds in which the nitroglycerine is produced and of those where it is treated in the liquid state are covered with sheet-lead with raised edges so that the material may be caught in case of breakage.

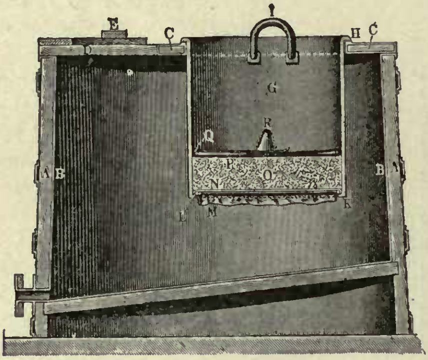

Fig. 198.

Where the nitroglycerine is worked in a pasty state (for dynamites) the flooring is of wood free from crevices.

If nitroglycerine is accidentally spilled, it should be immediately wiped up with sponges.

The channels through which nitroglycerine passes from one shed to another are in the form of gutters furnished with removable covers and are fitted with a longitudinal pipe through which warm water may be circulated in winter and the danger of freezing avoided. A disadvantage attending the use of these channels is that an explosion in one shed is propagated along the channels to all the other sheds. Hence the precaution is taken of disconnecting one section of a channel when not in actual use. In many factories the nitroglycerine is transported in rubber pails (*see above*).

The windows of the sheds are smeared with whitening, as the presence of curved parts in the naked glass might possibly result in the focussing of light on the explosive material and in the explosion of the latter.

USES OF NITROGLYCERINE. Small quantities are sometimes used in medicine to induce dilation of the blood-vessels, but practically the whole of the production is used as an explosive. In America it has been long in use in the pure state for large mining operations; Mowbray freezes it and transports it in large quantities on trains from the factory to the place of consumption, as he regards it as less sensitive in the frozen state, but this view is generally contested. It has also been transported without danger in solution in methyl or ethyl alcohol, from which it is reprecipitated with water at its destination. Almost all the nitroglycerine made is used in the manufacture of various kind of dynamites, dynamite gelatines, explosive gelatines, smokeless powder, etc.

DYNAMITES. This generic name is given to explosives obtained by gelatinising or absorbing nitroglycerine by various other substances. We have already mentioned that Alfred Nobel, the father of dynamite, had from 1860–1864 various explosions of nitroglycerine, sometimes of that recovered from the alcohol in which it had been transported (*see above*). In his attempts to diminish the dangers of nitroglycerine by diluting it with inert substances, Nobel discovered in 1866 that it is absorbed by *kieselguhr* (*infusorial earth*)[1] in considerable proportions (up to 81 per cent.), and that in this state its power is diminished but little, while it can be safely handled and transported. He found further that this *dynamite* is exploded only by means of a fulminate of mercury cap.

If the absorbing substances are inert, like infusorial silica (kieselguhr), sawdust, cellulose, etc., they form *dynamites with inactive absorbents,* which contain about 72 to 75 per cent. of nitroglycerine, 24·5 per cent. of kieselguhr, and 0·5 per cent. of soda for the No. 1 quality, and less nitroglycerine (up to 50 per cent.) in the Nos. 2 and 3 qualities.

In the new types of dynamite, however, the solid matter consists of active substances, *e. g.*, nitrocellulose, which take part in the explosion. These are *dynamites with active absorbents,* the absorbents or bases being again divided into *nitrates* or *inorganic oxidising bases* and *organic nitro-absorbents* (collodion-cotton, etc.).

I. MANUFACTURE OF DYNAMITE WITH INACTIVE ABSORBENTS. The kieselguhr used must be suitably prepared. It is first spread out in furnace chambers and gently heated to eliminate moisture and organic matter, and is then more strongly calcined in reverberatory or muffle-furnaces, excessive heating being avoided, as it may destroy the absorbing properties. It is then ground to fine powder and sieved. The flour thus obtained should not contain more than 1 per cent. of moisture and should be immediately filled into sacks and consumed the same day, as otherwise it might absorb moisture. It consists of silica with traces of oxides of iron and aluminium.

The nitroglycerine is weighed in buckets of hard guttapercha or lacquered wood and

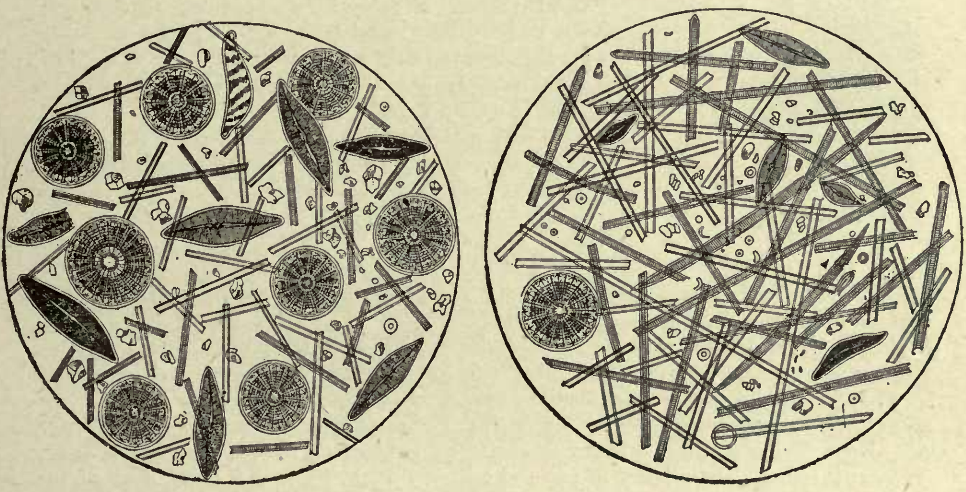

Fig. 199.

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[1] **Kieselguhr** is found in a very pure state in the Lüneburg moors, near Unterlüss in Hanover, at Oberhohe near Ebsdorf (Prussia), at Tütelwiese near Berlin, at Bilin (Bohemia), and in an inferior quality in Scotland, Norway, and Italy. It consists almost exclusively of the siliceous remains of diatoms, and contains also traces of iron and organic matter. It is unsuitable if it contains aluminium sulphate. Its particles are formed of empty tubes perforated in all directions, and it is this structure which renders kieselguhr so highly absorbent. Under the microscope, it presents the appearance shown in Fig. 199. At the present time kieselguhr dynamite has been almost entirely replaced by new types (gums or gelatines) described later.

The kieselguhr of Algeria (Orano) forms one of the richest deposits known, its composition being moderately constant, as is shown by the following percentage compositions of two samples (1911):

	H_2O	SiO_2	NaCl	$CaCO_3$	$MgSO_4$	Impurities
Orano type . . .	5·7	72·6	0·3	14·8	2·2	4·2
Cherchell type . . .	6·1	80·4	0·2	4·4	1·6	8·1

In 1914 a deposit of a million tons was found in Chili.

is carefully taken to the *mixing-house*, where it is poured into wooden troughs lined with sheet-lead, and containing the absorbent. Skilled workmen then mix the mass rapidly by hand; sometimes rubber gloves are worn, but usually the men prefer to do without gloves, as the hands become accustomed to the action of the nitroglycerine in two or three days.

It is important to obtain a homogeneous mixture, so that not the least portion of the kieselguhr remains free from nitroglycerine. After this hand-mixing the mass is rubbed through brass-wire sieves (2 to 3 meshes per centimetre) arranged above lead-lined wooden troughs. The dynamite is placed on the sieve with a wooden spatula and pressed through with the palm of the hand; here, too, the use of rubber gloves is not popular with the operatives. In the troughs the dynamite is in the form of fine grains, which should not be too dry or too *greasy*. If too dry, it is passed again through the sieve or mixed with more nitroglycerine, whilst if too greasy it is mixed with a further amount of kieselguhr. It is then placed in small portions in rubber bags or in wooden boxes lined with sheet-zinc and is removed to the building where the cartridges, used especially in mines, are prepared. Here the dynamite is transformed by simple presses into rolls, 19, 23, or 26 mm. in diameter. A very simple press devised by O. Guttmann is shown in Fig. 200. The dynamite is introduced into the cloth bag, *m*, and falls into the tube, *l*, being pressed into this by the lignum vitæ or ivory piston, *p*, at the end of the bar, *d*, which is actuated by the lever, *i*; the cylinder of dynamite issuing from the bottom of the tube, *l*, is broken by hand into definite lengths, which are wrapped in parchment paper or waxed paper. The ordinary length is 10 cm. (discharge cartridges) or 2·5 to 5 cm. (primers). These cartridge machines are sometimes worked by pulleys and motors. In some cases the *boudineuses* illustrated later are used. After the dynamite is wrapped up, packets of 2·5 kilos are placed in cardboard boxes, which are wrapped and tied round and filled in tens into wooden cases. For military purposes the cartridges are put directly into metal boxes with a socket in the lid for inserting the detonator. For use under water these metal boxes are sometimes used, and sometimes sausage-skins or rubber bags.

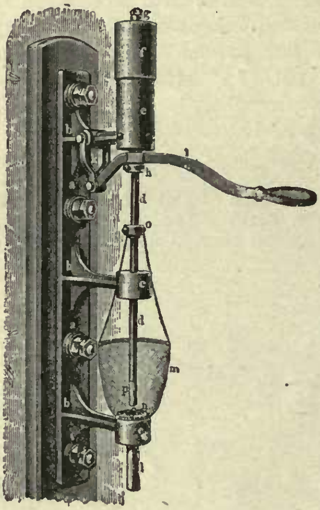

Fig. 200.

These cartridge buildings are usually small, with light walls and roof; only two or three operatives work in each, high earthen banks separating one building from the next, so that the effects of an explosion may be mitigated.

Dynamite containing 70 to 75 per cent. of nitroglycerine is known commercially as *dynamite No.* 1 and those with 50 per cent. and 30 per cent. as *No.* 2 and *No.* 3 respectively.

In place of kieselguhr various other absorbents are used at the present time, *e. g.*, wood meal (*cellulose*) mixed with inert mineral salts (calcium carbonate, sodium bicarbonate, etc.).

First in America and then in Austria *fulgurite* was prepared with 60 per cent. of nitroglycerine, the remaining 40 per cent. consisting of wheaten flour and magnesium carbonate. At Cologne, Müller prepared a *Wetter-dynamite* (*safety dynamite*, for use in mines containing firedamp; *see later*) by mixing 10 parts of ordinary dynamite with 7 parts of crystalline sodium carbonate; the water-vapour formed on explosion surrounds the flame and the explosive gases and thus prevents explosion of the firedamp. Many varieties of these dynamites are used to a greater or less extent in practice, *e. g.*, carbodynamite, containing 90 per cent. of nitroglycerine and 10 per cent. of carbonised cork, *sebastine*, *lithoclastite*, *carbonite*, etc. (*see later*, pp. 307, 311).

Properties of Dynamite with Inert Bases. This forms a pasty mass of reddish yellow, red, or grey colour according to the quality of the infusorial earth employed; to ensure a uniform colour about 0·25 per cent. of burnt ochre is often added. It is odourless and has the sp. gr. 1·4 and the pasty consistency of wet modelling clay; the inside of the wrapper should show no traces of nitroglycerine (sweating). It is much less sensitive to pressure and percussion than nitroglycerine and, in small portions, may be lighted and burned without exploding.

It can, however, be exploded by powerful percussion or detonation, or by red-hot metal, or by heating suddenly to a high temperature or for a long time at 70° to 80°. Dynamite freezes at temperatures below + 8° and then becomes less sensitive; before being used it must be carefully thawed in warming-pans, surrounded by water at a temperature not exceeding 60°; it must never be thawed on a heated metal plate. Thawed dynamite should be used carefully, as a little nitroglycerine exudes during thawing. Most of the dynamite made is used as an explosive in mines and for firearms; for cannon it has little use, owing to the danger caused by sweating during the thawing, so that for military purposes explosives are used which are safer to transport and not so sensitive to shock or to discharge (explosion by influence).

For non-congealing dynamites, *see* note on p. 276.

II. **DYNAMITES WITH ACTIVE BASES.** (*a*) **Pulverulent Dynamites with Inorganic Nitrates.** Immediately after the discovery of dynamite with a silica base came the idea of replacing the inactive substance, which diminished the force of the nitroglycerine, by active substances, so that the explosive power of the dynamite might be increased.

In America such dynamites are often made with 40 per cent. of nitroglycerine, 45 per cent. of sodium nitrate, 14 per cent. of wood-pulp, and 1 per cent. of magnesium carbonate; these dynamites are well suited for mines where no great power but considerable safety is required. In Europe mixtures of nitroglycerine, ammonium nitrate, fine sawdust, sodium nitrate, carbon, etc., are made; *e. g.*, 20 per cent. nitroglycerine, 36 per cent. sodium nitrate, 25 per cent. ammonium nitrate, 18·5 per cent. roasted rye flour, and 0·05 per cent. soda.

In Austria Trauzl in 1867 prepared a pasty mixture of nitroglycerine with guncotton, which was not affected by water and was exploded only by fulminate of mercury detonators. This product was not successful, but similar and improved preparations were subsequently made.

About this time Abel in England prepared *glyoxiline* by soaking defibred guncotton and potassium nitrate in nitroglycerine; this also was unsuccessful.

(*b*) **Blasting Gelatine and Gelatine Dynamite.** Since these contain nitrocellulose, they will be mentioned later (*see* Smokeless Powders, p. 294), after the manufacture of nitrocellulose has been described.

Statistics of dynamite: *see later*, at the end of the chapter on Explosives.

Various attempts have been made, but without practical success, to use nitro-derivatives of carbohydrates as explosives. Mention may be made of: **nitromannitol**, discovered almost simultaneously early in 1847 by Flores Domont and Ménard and by Ascanio Sobrero, who named it *fulminating mannitol* and obtained it in a similar manner to nitroglycerine. It is composed mainly of *hexanitromannitol*, $C_6H_8(ONO_2)_6$, which consists of white crystals melting at 112° to 113°, while the crude product, containing tetra- and penta-nitromannitols, melts at 80°; it dissolves to some extent in alcohol (1·35) and better in ether (1·24), and has the density 1·6 or, when compressed, 1·8. It is a shattering explosive, highly sensitive to shock.

NITROSTARCH could not formerly be obtained sufficiently nitrated, but *octonitrostarch*, $C_{12}H_{12}O_{10}(NO_2)_8$, containing nearly 16·5 per cent. of nitrogen, may be prepared by the process of Hough of New York (Ger. Pat. 172,549, 1903, improved later); this consists in treating the starch with a mixture of 3 parts of 95 per cent nitric acid, 2 parts of 98 per cent. sulphuric acid and sufficient SO_3 to yield an anhydrous mixture containing 2 per cent. of free SO_3, a further quantity of oleum with 2 per cent. of free SO_3 being added during the nitration. It appears that nitrostarch was tried as a military explosive in the United States prior to the European War.

NITROCELLULOSE

(Guncotton or Pyroxyline and Collodion-Cotton)

This substance should, to be in order, be described later, after cellulose (which is a carbohydrate with many alcoholic groups and with a molecular formula polymeric with $C_6H_{10}O_5$) has been studied, but as its properties and uses are closely connected with those of explosives, it is considered opportune to include it in the present section.[1]

CONSTITUTION OF NITROCELLULOSE. The relation $C_nH_{2m}O_m$ of the components of cellulose being expressed by the more simple formula $(C_6H_{10}O_5)_n$ it is found that the maximum degree of nitration consists in the introduction of three nitric acid residues per molecule of $C_6H_{10}O_5$, so that *guncotton* was given the name *trinitrocellulose,* and was represented by the formula $C_6H_7O_5(NO_2)_3$. Since the use of more dilute acids results in the combination of a less proportion of nitric acid residues, it is supposed that a *mononitro-* and a *dinitro-cellulose* are also formed.

It was found later by Eder that there exist nitrocelluloses with compositions intermediate to those of tri- and di-nitrocelluloses, and others between the mono- and di-nitro-compounds, so that it must be supposed that cellulose has a formula at least double that of the simple one given above, but the mononitrocellulose corresponding with this doubled formula $C_{12}H_{20}O_{10}$, *i. e.*, $(C_6H_{10}H_5)_2$, has not yet been prepared.

Still later Vieille, by accurate study of the nitrocelluloses prepared with acids of various concentrations, succeeded in preparing eight different types of nitrocellulose, this result indicating that Eder's formula, which predicted only six, could no longer serve. Vieille then proposed for cellulose a formula double that of Eder, *i. e.*, $C_{24}H_{40}O_{20}$ or $(C_6H_{10}O_5)_4$, according to which twelve nitrocelluloses are theoretically possible; eight of these, from endeca- to tetra-nitrocellulose have been actually prepared. Mendeléev, having found nitrocelluloses intermediate to or identical with these twelve, but different from those studied by Vieille in being soluble in a mixture of alcohol and ether, proposed the doubling of Vieille's formula, so that cellulose becomes $C_{48}H_{80}O_{40}$ or $(C_6H_{10}O_5)_8$. To-day, however, it is thought that these differences are due to mechanical mixtures of the various nitrocelluloses rather than to separate chemical compounds, and further, that the nitration is gradual and leads from the more simple to the more complex forms.

[1] In 1833 Braconnot observed that when starch or wood is treated with concentrated nitric acid, a mucilaginous solution is obtained which, on addition of water, yields a white powder soluble in a mixture of alcohol and ether; this powder, which burns vigorously, he called *xyloidin.*

In 1837, by immersing cellulose (flax, cotton, paper, etc.), for a few seconds in concentrated nitric acid and washing it immediately with a large quantity of water, so that it retains its original fibrous form, Pelouze obtained a product which is highly inflammable and explodes on percussion; he regarded it as xyloidin (in reality it was guncotton), and recommended it for making fireworks.

In 1846, Schönbein at Basle, and some months later, and independently, Böttger at Frankfort discovered that the nitration of cellulose takes place much more easily and completely if the cotton is treated with a mixture of concentrated nitric and sulphuric acids (industrially this method was used in 1846 by Hofmann and by Muspratt). In order to utilise industrially the guncotton thus obtained, the two discoverers combined and kept their process secret. After the initial difficulty in getting this new explosive taken up in practice, the extraordinary power of guncotton and its great advantages over black powder aroused considerable enthusiasm. Scarcely, however, had it come into general use in various countries than a number of *spontaneous* and fatal explosions in *guncotton* factories and magazines, by which whole buildings were razed to the ground, created such a panic that its manufacture was everywhere abandoned. The process of nitration was then already known to Knop and Karmarsch, and to others, who manufactured guncotton by this simple process. In 1846, Sobrero made use of the nitric-sulphuric mixture for the preparation of nitroglycerine.

In 1853, the Austrian, Captain von Lenk, ascertained how to render guncotton safe. The Austrian Government acquired from Schönbein and Böttger the process of manufacture (at a price stated to be 30,000 florins, or £2500) and maintained the secret of avoiding the spontaneous decomposition of guncotton until 1862. Then von Lenk communicated the secret to the French and English Governments, and in 1864 patented the process in America. Whilst in America the manufacture was undertaken on an enormous scale, in Austria and England it was again suspended on account of further terrible explosions in the factories themselves; these were explained by the English workers as due to the insufficient purification of the nitrocellulose by von Lenk. In 1865, Abel discovered the method of bestowing absolute safety and keeping qualities on the nitrocellulose. He used first of all the process of washing proposed in 1862 by the Englishman J. Tonkin, which consisted simply in complete washing with abundant supplies of water; the nitrated cotton was then defibred or *pulped* in " hollander " machines similar to those employed in paper factories and the wet pulp subjected to considerable pressure. From that time the manufacture extended to all countries, in spite of an English factory being blown up in 1871 (apparently a criminal act), and in recent times it has acquired new and increased importance owing to the discovery of smokeless powder.

The process universally used at the present time in the manufacture of guncotton is that indicated by Abel. Before the discovery of smokeless powder, guncotton had limited applications and was not used in mines, since, in the form in which it was prepared, it had an excessive shattering action, whilst in mines progressive explosives are usually required.

Nitrocelluloses with more than 12·83 per cent. of nitrogen were at one time regarded as being insoluble in alcohol-ether, but Abel showed that there are nitrocelluloses with 13·2 per cent. of nitrogen and still soluble in this mixture, whilst others with only 12·8 per cent. are insoluble, and that this depends on the method of preparation—the duration of action of the mixed acids, the ratios and concentrations of the latter, and the temperature at which they act—and on the nature, purity, and dryness of the cotton. Only by following exactly the directions is it possible to obtain a constant percentage of nitrogen and complete solubility or insolubility in the mixture of alcohol and ether.

It was also once thought that guncotton was a *nitro-compound* in the true sense of the word, *i. e.*, that the NO_2 groups were united directly to carbon, but first Béchamp and then others showed that it is a true nitric ester which can be saponified, with regeneration of the cellulose, by alkalis, alkaline salts, ammonium sulphide, or ferrous chloride. It has been further shown that with the maximum of nitrogen an oxynitrocellulose is obtained [oxycellulose is $(C_6H_{10}O_5)_3 + (C_6H_{10}O_6)_n$, so that the nitrocellulose will be $C_6H_7(NO_2)_3O_5 + C_6H_7(NO_2)_3O_6$, and this with ferrous chloride gives oxycellulose; nitromannitol, treated similarly, gives mannitol and not oxymannitol].

PROPERTIES OF GUNCOTTON. Under the microscope nitrocellulose has the same appearance as ordinary cotton, but in polarised light it appears iridescent. When moistened with a solution of iodine in potassium iodide and then with sulphuric acid, nitrocellulose becomes yellow and cellulose blue. It is somewhat less white than ordinary cotton, is rather rough to the touch and crackles when pressed with the fingers; it becomes electrified when rubbed and then appears phosphorescent in the dark. It is soluble in ethyl acetate (as shown by Hartig in 1847), nitrobenzene, benzene, acetone, etc., but insoluble in water, alcohol, ether, acetic acid or nitroglycerine, although a mixture of nitroglycerine and nitrocellulose is soluble in acetone, forming a jelly, *cordite* (*see later*).

It resists the action of dilute acids, but is decomposed slowly by concentrated sulphuric acid or hot alkali, and is completely dissolved by hot sodium sulphide. Decomposition is also effected by iron and acetic acid or by ammonium sulphide or ferrous chloride (Béchamp).

Flocculent, *loose* guncotton has the sp. gr. 0·1, whilst the powder (pulp) has the sp. gr. 0·3 and is exploded by shock or percussion only at the point where it is struck, the explosion not being propagated to the whole mass. When ignited, it burns so rapidly that even when it is placed on black powder, the latter does not burn.

In the form of cord, it burns more slowly and may be used as a rapid fuse. When wet or compressed it has a specific gravity varying from 1 to 1·3 (the absolute sp. gr. is 1·5) and it then burns slowly and cannot be exploded by percussion or by ordinary detonators; explosion can, however, be induced by detonating a little dry guncotton with a fulminate of mercury cap. The shattering power diminishes with increase of the density, which reaches a maximum on gelatinisation (*see later:* Progressive Smokeless Powders). The decomposition proceeds according to the equation:

$$2C_6H_7O_2(ONO_2)_3 = 5CO + 7CO_2 + 8H + 3H_2O + 6N.$$

Less compressed guncotton gives more CO and H in comparison with the CO_2 and H_2O, and hence has a less effect, the development of heat being smaller. No ash or smoke is formed, and 1 kilo of guncotton yields 741 litres of gas (the water being liquid, or 982 litres if the water is in the state of vapour), which is inflammable and, owing to the presence of carbon monoxide, poisonous. The temperature of combustion has been given as 6000° (*i. e.*, 1071 Cals. is developed by 1 kilo), and in practice exceeds 4000° and may produce a pressure of 15,000 atmos.

Unless guncotton is carefully prepared, it undergoes gradual change and may explode spontaneously, especially in the light, and to this are probably due the great explosions which occurred formerly (1848–1862). Even dry, granulated guncotton becomes harmless and safe to handle if it is immersed for a moment in ethyl acetate, as it becomes coated with a gelatinous layer which dries and preserves it, if moist, from further evaporation.

Guncotton is transported in large quantities in the wet state in wooden boxes placed in others of zinc which are sealed hermetically to retain the moisture. It is stored in dry magazines which are situate at least 150 (better 500) metres from any habitation and are not surrounded by earthworks so that the more serious effects due to projection of *débris* may not be added to those of an explosion

MANUFACTURE OF GUNCOTTON. Hanks of purified cotton, free from impurities, are employed. This cotton should fulfil certain requirements.[1]

In place of cotton it is economical in some cases to use filter-paper, unsized paper, parchment paper or paper cellulose, but such substances are less convenient than cotton as they easily undergo pulping to an almost pulverulent mass, which leads to losses and requires different conditions for nitration.

The *pure* cotton is placed loose on trays which are arranged in a drying-stove heated by means of gilled pipes through which steam circulates; the heating is continued until the proportion of moisture is less than 0·5 per cent., after which the cotton is allowed to cool for twelve to fifteen hours in hermetically sealed boxes. If not pure the cotton is best defatted by boiling it for two to three minutes with 2 per cent. sodium hydroxide solution; it is then washed with water and subsequently treated with very dilute nitric acid in the hot. In some cases it is also bleached with a weak solution of hypochlorite, well rinsed with water and dried in a hot-air oven at 100° to 115° as above. When almost dry it is carded, dried completely, and, while still hot, placed in hermetically sealed boxes so that no more moisture may be absorbed.

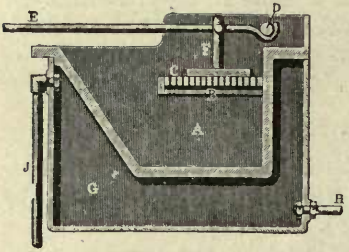

FIG. 201.

Nitration is then effected with a mixture of concentrated nitric and sulphuric acid, as follows: 3 parts of pure sulphuric acid of sp. gr. 1·840 (95·6 per cent.) are poured into 1 part of pure nitric acid of sp. gr. 1·500 (95 per cent.), mixing taking place immediately and completely without the aid of stirrers. In this way a mixture containing about 72 per cent. of H_2SO_4, 23·5 per cent. HNO_3, and 4·5 per cent. H_2O is obtained. If the acid mixture contains much nitrous acid, it may yield *cellulose nitrite*, which contains only 2·5 per cent. of nitrogen, is insoluble in acetone and is less stable than ordinary nitrocellulose (Nicolardot and Chertier, 1910).

The mixture is then delivered with the help of an acid elevator (*Montejus*) into the nitration apparatus, consisting of a cast-iron vessel, *A* (*dipping pot*) (Fig. 201), standing in a larger vessel, *G*, through which cold water circulates from *H* to *J*. The cotton is immersed in small portions (300 to 800 grams) in the acid-bath and is stirred with an iron fork. In England 1 kilo of cotton is used per 160 kilos of the acid mixture, while in Germany 1 kilo of cotton is taken for every 40 kilos of acid; after a short time (fifteen to thirty minutes) the nitrated cotton is removed with iron forks and is placed to drain on a cast-iron grid

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[1] *Cotton* for nitrocellulose should be pure white and should not contain dust or fibres of jute, hemp, or flax, or woody matter or pods; these impurities, when separated by hand from 200 grams of the cotton, should not exceed 0·5 gram. The filaments should not be too short, otherwise they form a paste during nitration. A small piece thrown into water should sink in two minutes. It should not contain more than 0·9 per cent. of substances soluble in ether (fats, etc.); in many factories 0·5 per cent. is not allowed. In England the amount of fat allowed is 1·1 per cent. extracted with ether in four hours in a Soxhlet apparatus (*see* Analysis of Fats). The moisture, determined by heating the cotton in an oven at 100° until its weight remains constant, should not exceed 6 per cent. and the cotton merchant is debited with any excess and also with the cost of drying.

When moistened with a few drops of water, the cotton should maintain a neutral reaction.

The ash, estimated by heating a few grams of the cotton to redness in a platinum capsule until it becomes quite white and of constant weight, should not amount to more than 0·3 per cent.

(grate), *B* and *C*, arranged on one side above the vessel; before it is taken away, it is pressed with a cast-iron plate, *F*, connected with a lever, *D E*.

The acid mixture is renewed when it has treated 30 to 50 per cent. of its weight of cotton; also after each portion of cotton is removed from the bath, fresh acid mixture, equal to ten times the weight of the cotton taken out, is added in order to make up for what has been absorbed and combined. On the German system (where less acid is used) renewal takes place more frequently. Above each of the nitrating vessels is a hood with a strong draught to carry off the nitrous vapours which are always evolved. Excessive rise of temperature or use of weak acid mixtures (with more than 9 per cent. of water) gives a guncotton which contains less nitrogen and is not completely soluble in alcohol-ether, as is required in practice.

In some factories the nitration is carried out in a number of small, deep and narrow, hemispherical vessels of cast-iron mounted on trolleys. These are charged in order with certain weights of acid mixture (30 to 50 kilos) and dry cotton (2 to 4 kilos), and, after thorough mixing, the trolleys are pushed into an oblong lead-lined chamber provided with as many doors as there are trolleys. A powerful aspirator draws the nitrous vapours into a wooden flue. A battery of soaking-pots is used in such a way that when the last is introduced into the chamber the first has already finished reacting (thirty to forty minutes), and as the pots are of metal and relatively small and are in a strong draught, the heat developed is readily dispersed. The pots are removed from the chamber and taken to the neighbouring centrifugal machines, into which the contents of the pots, which are mounted on pivots, are tipped. The centrifuges are similar to those employed in sugar factories (*see* Sugar) and have a steel or leaded steel rotating basket; aluminium ones have also been tried, but not with great success. A few minutes' centrifugation at 900 to 1000 revolutions per minute removes the greater part of the acid from the guncotton; the latter is immediately taken to the washing machines, while the acid recovered is revivified in the manner described on p. 280. If drops of water or lubricating oil fall on to the cotton during centrifugation, the mass sometimes undergoes sudden decomposition with formation of a dense cloud of brown vapour; this does not constitute a serious danger, since usually it is not accompanied by explosion.

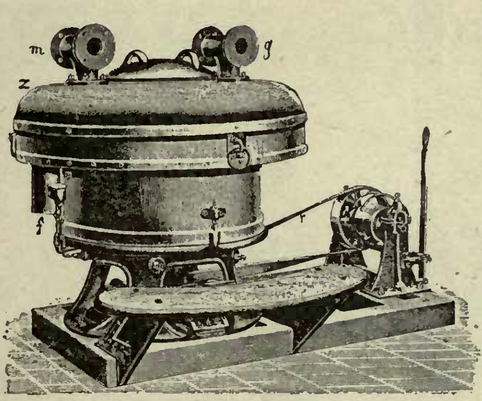

FIG. 202.

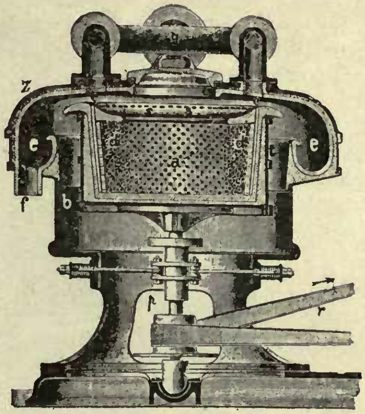

FIG. 203.

In some factories the nitration is nowadays carried out directly in the centrifuges, which may be of naked or leaded steel or even of earthenware, although these are heavier and more fragile (*see* Figs. 202, 203). The latter consist of a double-walled earthenware basket, the inner wall, *d* and *a*, but not the outer one, being perforated; the two walls being a slight distance apart, an annular space, *c*, is left, which has an outlet above in a number of holes, *s*, in the edge of the bush. The whole is bound with steel hoops, *t*, to prevent danger from projection in case of fracture. The dry cotton (7 to 8 kilos or more) is arranged peripherally inside the perforated basket, the acid being supplied by the tube, *m*; the basket, surrounded by the jacket, *b*, and the cover, *z*, both of earthenware, is set in motion by the shaft, *p*, driven by the belt, *r*. The acid is driven uniformly through the cotton by centrifugal force, rises through the ring space, *c*, and issues from the holes, *s*, into the channel, *e*, whence a pipe, *f*, carries it to an elevator to be circulated again. The operation is of short duration, and the red vapours are emitted from the tube, *g*. During nitration, the velocity of the drum is relatively low, but at the end the velocity is increased; the nitrated cotton can then be taken away at once to be washed.

Use is, however, preferably made of steel centrifuges with circulation of the acid, as proposed by Selwig and Lange; the basket, *d*, is perforated (Fig. 204) and the cover is of aluminium and hinged, and is furnished with a large tube, *o*, communicating with the pipe of an aspirator, *n*. The basket is moved slowly and filled with the nitric-sulphuric mixture (*e. g.*, 70 per cent. H_2SO_4, 23 per cent. HNO_3 and 7 per cent. water) up to the top edge; the cotton is then introduced in packets (1 kilo per 40 to 50 kilos of acid) and the basket given a velocity of 20 to 30 turns per minute. This movement causes the acid to circulate continuously through the cotton, and in half an hour the nitration of 6 to 8 kilos of cotton is complete; the acid is then discharged and the velocity increased to remove as much acid as possible from the cotton, which is taken out and washed in the ordinary way. Use is now made of centrifuges 1 to 1·1 metres in diameter, and 14 to 18 kilos of cotton are nitrated at a time.

Sometimes, especially in summer, the nitrocellulose decomposes in the centrifuge itself, producing vast columns of reddish-brown vapour; as a rule, not explosion, but merely deflagration occurs. Such decomposition takes place the more readily at the end of the centrifugation, especially if this is unduly prolonged or excessively rapid; often the cause is the spurting of water or lubricant into the centrifuge, but it may be the presence of impurities in the cotton or a workman spitting into the centrifuge.

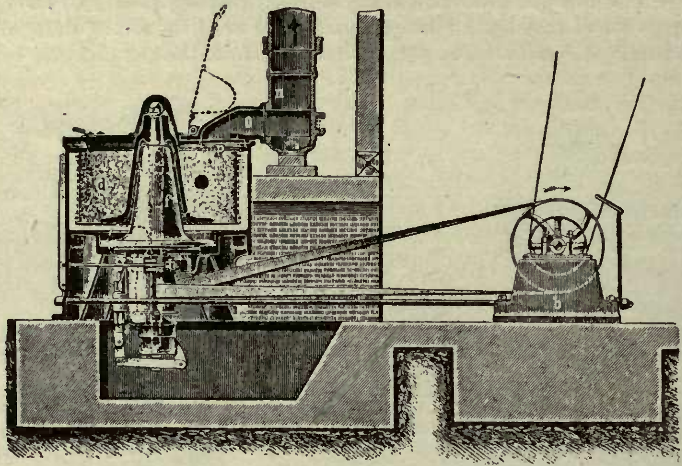

FIG. 204.

Since August 1905 in the Royal Gunpowder Factory at Waltham Abbey (where 2000 tons are produced per annum), guncotton has been made by the *displacement process* of J. M. and W. Thomson, improved by Nathan, which is briefly as follows (Ger. Pat. 172,499, 1904).

Into the earthenware basins, which have perforated double bottoms and aluminium covers (Fig. 205) and are connected in groups of four by means of leaden pipes and also communicate with an exhauster, G, 600 litres of the nitric-sulphuric mixture is placed; about 10 to 12 kilos of cotton is then introduced in small portions into each vessel and pressed with perforated stoneware discs divided into septa so that the acid exactly covers the cotton and scarcely fills the orifices of the discs; a layer of water about 1 cm. deep is then cautiously introduced on to the perforated disc, which separates the cotton and acid from the superposed water and thus prevents the two liquids from mixing, the fumes being largely absorbed by the water.

The nitration lasts about two and a half hours, and at the end water is introduced above the perforated plate, this displacing at the bottom a corresponding quantity of the acid; the acid thus recovered (90 per cent.) is reinforced with oleum and strong nitric acid. The displacement lasts three hours, after which the mass is centrifuged and the cotton washed, rendered stable, pulped, etc.

Since guncotton should have a very definite nitrogen content, different from that of collodion-cotton used to gelatinise nitroglycerine (*see later*), the process of nitration is carefully followed by numerous rapid analyses until suitable conditions are found for obtaining a constant product; after this has been done, the final control is sufficient. It has been proposed to follow the extent of nitration of cellulose by observing its behaviour towards polarised light. In recent years it has been shown that guncotton of more constant type and more readily rendered stable is obtained if the acid mixture is renewed for each nitration; the last processes described are hence to be preferred.

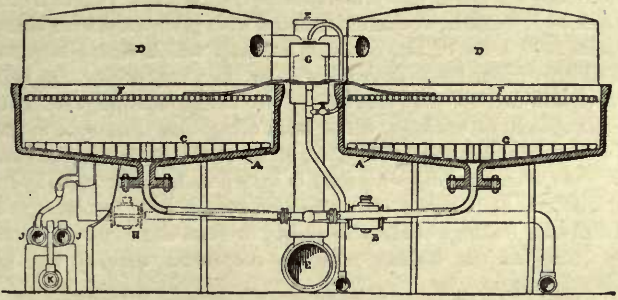

FIG. 205.

There has been much discussion concerning the relative suitability of centrifuges and Nathan-Thomson vessels for nitration. It now seems established that, even in the latter, either guncotton or collodion-cotton may be prepared, provided that the conditions of the reaction, the temperature, the time, and the concentration and composition of the acids are suitably and thoroughly studied. The plant of a works using centrifuges is the more expensive, requires the greater upkeep expenses and contaminates the air with acid fumes.

The nitrocotton obtained by the Thomson process is the more stable, since the displacement of the acid by water is accompanied by slight heating, which allows of the decomposition of the unstable secondary products and the elimination of the sulphonitric cellulose.

For the economical working of the Thomson process, the earthenware vessels must be of good quality, so as to avoid breakages; such vessels are now easily procurable. With the centrifuge system concentrated acid is recovered, but part of it is lost; with the Thomson vessels the whole of the acid is recovered, but about 25 per cent. of it is diluted with 20 to 25 per cent. of water and has to be denitrated.

FIG. 206.

The degree of nitration and the stability of nitrocotton may be estimated by measuring the viscosity of its solutions, nitro-oxycelluloses giving more fluid solutions than nitrocellulose. Nitro-oxycellulose has little stability and is formed from cotton which has been highly bleached with chlorine prior to nitration (Piest, 1913).

The theoretical *yield* of dry guncotton is 185 kilos per 100 kilos of dry cotton; in practice 170 to 175 kilos is obtained.

WASHING. The nitrocellulose from the centrifuge is passed directly into the oval washing vessel (*see* Fig. 206), which has a longitudinal partition down the middle (like the hollander machines used in paper-making), and in which a shaft furnished with beaters mixes the whole mass with water; the latter is constantly renewed and the washing continued until the acid reaction towards litmus paper disappears (two to three hours). The washed guncotton is either centrifuged again or put to drain in wooden baskets. Although it no longer exhibits an acid reaction, yet, as was shown by J. Tonkin in 1862 and by Abel in 1865 (in England), it still contains acid, or rather unstable sulphuric esters, in the small channels of its fibres.

To separate these remaining traces of acid, the nitrocellulose is rendered stable by the Robertson system, which consists in boiling it for two consecutive periods of twelve hours each with water in wooden vats fitted with perforated false bottoms (one vat holds even more than 1000 kilos of the cotton), beneath which steam is passed. Then follow four more boilings of four hours each with water (formerly one or two boilings with calcium carbonate were also carried out), and finally two or three boilings each of two hours with fresh water. This system of washing, which lasts altogether thirty-six to forty-eight hours, is preferable to that in which the boilings are short at the beginning and long at the end, and especially to that where boiling with soda is interposed, as the soda hydrolyses the nitrocellulose and transform it partially into collodion-cotton poor in nitrogen and soluble in alcohol-ether. In France boilings of sixty to eighty or even one hundred hours are employed.

Some of the boiling may be dispensed with if the nitrocellulose is steamed in closed vats.

In 1911, Baschieri simplified the Robertson system by boiling the nitrocellulose (roughly washed and centrifuged) for two hours in 0·05 per cent. sulphuric acid solution, then washing twice in cold water, boiling for two hours with 0·1 per cent. sodium carbonate solution, and finally washing twice with cold water. By this method the nitrocotton is rendered ready for pulping with a minimum loss of nitrogen, the maximum stability being thirty-five minutes at 70° or, with the Abel test, 135°. The acid bath serves especially for the elimination of the unstable and soluble sulphonitric celluloses.

PULPING. In spite of all the washing and boiling to which it is subjected, the guncotton persistently retains a trace of acid, and to remove this, the cotton is thoroughly defibred (*pulped*) as was proposed by Tonkin and by Abel in 1865. This operation is carried out in hollanders similar to those used for the preceding washing and identical with those used in the manufacture of cellulose for paper (*see later*, section on Paper, for figures and cross-sections).

Pulping lasts from five to eight hours, according to the fineness required, but if it is incomplete, inconveniences are met with in the subsequent compression, the desired density not being attainable; also if pulping is carried too far, the compression is disturbed in another way. Guttmann proposed the use of hot water in pulping, and this possesses several advantages in addition to saving time. In the large hollanders, as much as 600 to 800 kilos of guncotton can be treated at one time. In some cases a little calcium carbonate is added to guncotton to preserve it and to neutralise any residual acid; it is added in powder just before the completion of pulping, but its use is not to be recommended, as it tends gradually to produce slight decomposition of the nitrocellulose.

STABILISING. Guncotton (and also collodion-cotton) thus prepared does not usually answer the rigorous tests to which it is subjected (*see later*, Tests of Stability), and is rendered stable by again boiling it for some hours with water in large wooden tanks (sometimes lined with lead), jets of steam, and also of air to keep the mass moving, being passed in for eight to twelve hours. By mixing in this way the nitrocottons from different nitrations, a mass is obtained which is perfectly homogeneous, even as regards nitrogen content, this being difficult to achieve otherwise.

In order to separate the water, the mass is placed in suitable centrifuges fitted with drums of fine metal gauze entirely surrounded by linen; in other cases, the water is separated as in paper-mills, by placing the mass in chambers having perforated brass floors covered with cloth, the pulp drained in this way being finally centrifuged. The water separated from the pulp is allowed to stand in suitable vessels to deposit the finer fibres it has carried away. After centrifugation, the pulp contains about 25 to 30 per cent. of water and in this state it can be kept safely in zinc boxes, in which it can be transported if it is slightly compressed and the cover of the box soldered; in moist wooden boxes or in paper wrapping nitrocotton readily becomes coated with mould. If properly prepared, guncotton should not contain more than 3·5 to 4 per cent. of collodion-cotton (soluble in alcohol-ether), but in England 7 to 8 per cent. is allowed. Excessively prolonged boiling increases the proportion soluble and lowers somewhat the nitrogen content; immoderate action of alkali produces a little hydronitrocellulose.

COMPRESSION OF GUNCOTTON. For military purposes, that is, for cartridges and for the blocks used for charging torpedoes, the still moist guncotton is strongly compressed, to render it safer and more powerful owing to the increased charging density (*see above*), which reaches the value 1·2 with pressures of 500 to 1000 atmos. or 1·35 with still greater pressure. Fig. 207 shows in section a Taylor and Challen hydraulic press used for this purpose; this is set up in an isolated room and can be controlled from a distance so as to avoid any great amount of damage in case of explosion during the compression, this mostly happening if any hard foreign body chances to be present in the guncotton.

To obtain the greatest density, the pulp is first washed with hot water and slightly compressed in the mould, *d*, by means of the lever, *h*, the water being drawn away under the perforated base, *c* (covered with steel gauze), by a pump connected with the tube, *b*. The partitions, *l*, are raised and the mould passed through an aperture in the wall, *M* (which serves as a protection for the workmen), and thus above the plate, *n*, of the hydraulic press; this plate is kept horizontal by four columns, *S′*. The mould is raised by the piston, *t*, of the press so that it is pressed against a die, *r*, fixed to the cover, *q*. This cover is held fast by the four columns so that the die penetrates the mould and compresses the cotton under a pressure of 800 to 1000 atmos. The degree of humidity after the compression is about 12 to 14 per cent., and at each operation a block of 1 kilo is made, the shape being adapted to that of the projectile. Thus compressed, guncotton is so hard and compact that it can be worked quite safely with the plane, saw, or boring tool, a fine jet of water being directed at the point where the cutting is taking place. To prevent compressed guncotton from losing moisture and from becoming mouldy, it is dipped in molten paraffin wax, or, better, it is immersed for a moment in ethyl acetate (or acetone), which dissolves a little nitrocellulose at the surface and forms a kind of impermeable varnish.

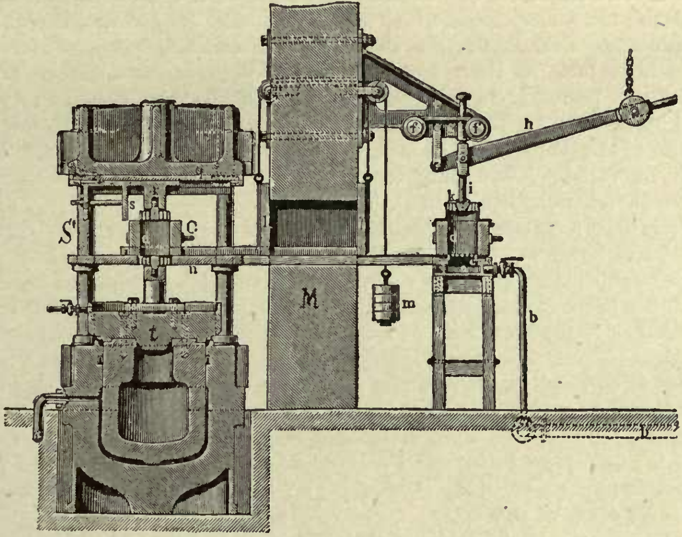

Fig. 207.

Since 1898, in some large works charges have been prepared in a single piece, either for grenades or for torpedoes, etc., by means of the powerful press devised by Hollings (Brit. Pat. 23,449, 1899).

USES OF GUNCOTTON. Until 1890, moist compressed guncotton had replaced all other explosives for the charging of torpedoes. It is used also for filling grenades, which are then covered with molten paraffin wax to unite the grenade and the explosive; explosion is effected by a detonator of dry guncotton. It is made also into compressed cartridges for use in mines, a cavity being left for the detonating cap and the fuse.

Since 1890, guncotton as a high explosive for military purposes has been replaced gradually and advantageously by picric acid and trinitrotoluene (T.N.T.), which are melted and poured directly into the projectiles, bombs, mines, etc. During the European War all the old stocks of guncotton were consumed, use being afterwards made solely of these aromatic nitro-derivatives and of various mixtures of them (*see later*).

Mixtures of granulated guncotton and nitrates are placed on the market under the names of *tonite, potentite,* etc. Abel obtained beautiful pyrotechnic effects by saturating guncotton with solutions of various mineral salts capable of imparting different colours to the flame. Guncotton is sometimes used for filtering acids, alkalis, and solutions of permanganate, being resistant to these reagents in the cold. Also it is employed in some cases as an electrical insulator and for bandaging purulent sores and wounds, being first saturated with potassium permanganate.

COLLODION-COTTON FOR GELATINE DYNAMITE, DYNAMITE, AND SMOKELESS POWDERS. During the last fifty years, a different, less nitrated nitrocellulose, *collodion-cotton*, has assumed very great importance in the manufacture of smokeless explosives. On the other hand, guncotton itself has, of late years, been largely replaced by compressed, crystalline, or fused *trinitrotoluene*, or by picric acid (*see* Part III), especially for military and naval purposes. Collodion-cotton was at one time thought to be dinitrocellulose, soluble in a mixture of alcohol and ether, but it has now been shown to be a mixture of various soluble nitro-compounds, which are formed under conditions different from those yielding guncotton. Collodion-cotton should have a constant nitrogen-content, and it should be readily soluble (to the extent of at least 95 per cent.) in a mixture of alcohol (1 part) and ether (2 parts), giving a dense viscous solution; this solubility may, however, be increased by prolonged heating under pressure with water acidified with sulphuric acid, which permits of the preparation, from this collodion-cotton, of artificial silk better than the Chardonnet variety (Chandelon, Ger. Pat. 255,067, 1911–1912). Collodion-cotton is soluble also in dichlorohydrin (p. 257).

If it answers these requirements, it gelatinises nitroglycerine well and dissolves completely in it; attention is, however, also paid to the time necessary for gelatinisation.

For photographic plates, extensive use was formerly made of ethereal-alcoholic solutions of soluble nitrocellulose (collodion), and in this case importance was attached not so much to the viscosity as to the proportion of nitrocellulose which would yield an elastic film of marked resistant properties. For this purpose, the nitration is carried out at a temperature of at least 40° to 50°, so that the resulting collodion is less viscous; also the nitrocellulose is not pulped.

The cotton is immersed for sixty minutes or longer in a mixture of 1 part of 95·5 per cent. sulphuric acid (sp. gr. 1·840) and 1 part of 75 per cent. nitric acid (sp. gr. 1·442) (this mixture contains 48 per cent. of H_2SO_4, 37·5 per cent. of HNO_3, and 14·5 per cent. of H_2O), at a temperature of about 40°.

The more concentrated the acid and the more prolonged its action, the higher will be the nitrogen-content, but the viscosity will not be decreased; a high temperature, however, results in diminution of the proportion of nitrogen and also of the viscosity.

More commonly nitration is carried out in the cold in the manner described for making guncotton, only the composition of the acid mixture being modified: with a content of 22 to 25 per cent. of nitric acid, guncotton is obtained if the acid mixture contains less than 10 per cent. of water and collodion-cotton if more than 10 per cent. of water (up to 15 to 18 per cent.), according to the desired nitrogen percentage and solubility in alcohol-ether.

To the International Congress of Applied Chemistry, London, 1910, Saposhnikov communicated a series of interesting investigations (1906–1909) on the practical conditions required to establish beforehand the type of the resulting nitrocellulose (percentage of nitrogen and solubility), the results being expressed as curves referred to triangular co-ordinates.

After nitration collodion-cotton intended for the manufacture of gelatine dynamite goes through all the operations of washing, pulping, and boiling employed with guncotton.

Collodion-cotton for gelatine dynamite or smokeless powder must be subjected to a *drying* process, while for smokeless powders the water is expelled in another way. Since the centrifuged pulp still contains 30 per cent. of water, whilst nitrocellulose begins to decompose at 70° (or even at 50° if badly prepared) and in the dry state is very sensitive to shock or percussion, the drying of collodion-cotton constitutes a very dangerous operation. At one time it was dried by means of indirect steam on iron plates heated to 40° to 50°, but, using the ordinary precautions, it may be dried on cloths in a current of warm air.

When dry, it sometimes becomes electrified on rubbing, or even by an air current, and this phenomenon explains the frequent spontaneous fires formerly occurring in the drying ovens. Guttmann prefers to dry the collodion-cotton on copper plates connected with the earth by wires (to discharge the electricity). These plates are perforated with conical holes 0·25 mm. wide at the top and 1 mm. at the bottom; strips of leather are used to prevent rubbing of the metal parts. In these ovens, the pulp is spread out and is subjected to the action of a current of air heated to 40° (in some cases, also dried: *see* p. 272), and in two days the mass is dry, not more than 0·1 per cent. of moisture being then present. The dried material is then carefully placed in rubber bags and stored in air-tight boxes.

The drying ovens are provided with alarm-thermometers, which also regulate the temperature automatically.

The workmen should wear rubber boots with copper nails and in the Waltham Abbey Factory the leather transmission belts are soaked in glycerine to prevent their electrification.

Drying in a vacuum is also employed (especially with fulminate of mercury and smokeless powders), and is then more rapid and takes place at a lower temperature, while the danger of an explosion is diminished owing to the absence of the tamping effect of the atmospheric pressure (*see* p. 264).

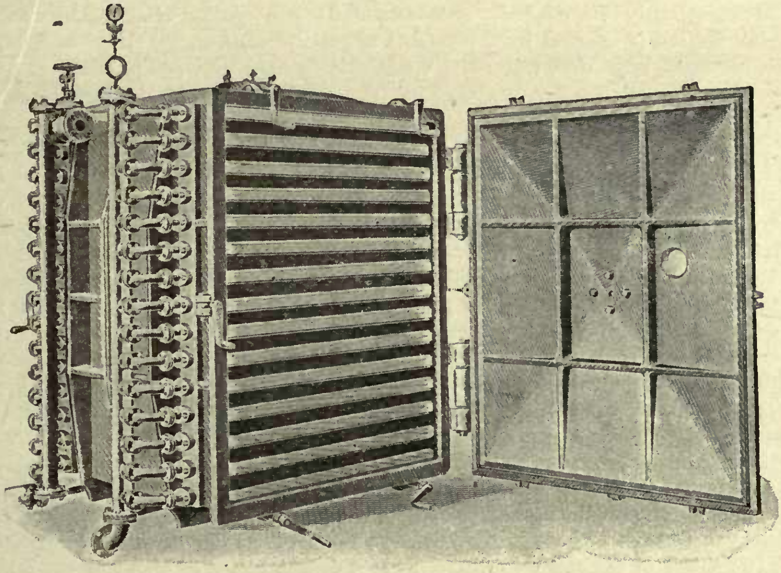

FIG. 208.

One of the commonest dryers working under reduced pressure is shown in Fig. 208; it is fitted with cloths and has double walls to allow of the circulation of steam, hot air, or hot water (*see also* p. 297).

Collodion-cotton for making ballistite (*see later*) should contain 11·75 to 11·95 per cent. of nitrogen, whilst that for ordinary gelatine dynamites contains as much as 12 per cent., almost completely soluble in alcohol-ether.

The distinction between collodion-cotton and guncotton on the basis of the percentage of nitrogen present is not a rigorous one, since it was shown by Roscoe (during the lawsuit in 1893 between the British Government and Nobel concerning the ballistite patent) that, by suitable modification of the quantity of water and of the ratio between the nitric and sulphuric acids in the nitrating mixture, a nitrocellulose which contains 12·83 per cent. of nitrogen and is soluble in alcohol-ether, or one which contains 12·73 per cent. of nitrogen and is insoluble, may be obtained.

SMOKELESS POWDERS. Even 50 years ago attempts were made to diminish the smoke produced by ordinary gunpowder by diminishing the amount of sulphur present, but its relations to the nitre and carbon cannot be greatly altered. Potassium nitrate was then replaced by ammonium nitrate, but this was found to be too hygroscopic; yet later, ammonium picrate was employed with better, but still not satisfactory, results. In 1864 Schulze prepared a smokeless powder from nitrocellulose obtained from pure wood-cellulose. It gave good results with sporting guns, but was too shattering for use in warfare, and the same was the case with a smokeless powder prepared in 1882 by Walter Reid by granulating nitrocellulose and gelatinising it superficially with alcohol and ether.

The true solution of this important problem is due to Vieille, who in 1884 found that the *shattering* action of guncotton could be transformed into a *progressive* (or *propellant*) action by destroying the fibrous structure with suitable solutions. To attenuate the rapidity of explosion of guncotton it must be made as dense as possible (theoretically the fibre free from interstices has the density 1·5), and this cannot be done practically with fibrous cotton (even when pulped) as a pressure of 4000 atmospheres would be necessary. Vieille, however, dissolved or gelatinised the nitrocellulose and then recovered it by evaporating the solvent; thus was prepared *powder B*, the first military smokeless powder.

With the smokeless powder prepared by Vieille in 1885 the velocity of projectiles from cannon was increased by 100 metres per second over that obtained with ordinary powder, the pressure in the cannon being the same in the two cases; hence guns of smaller calibre could advantageously be employed. This amounted to a revolution in the region of ballistics. The gelatinisation is effected by solvents of nitrocellulose, *i. e.*, by ether, acetone, ethyl acetate, nitroacetylglycerine, tetra- and penta-chloroethane, etc. (*see* p. 122).

SMOKELESS PROGRESSIVE POWDERS

SMOKELESS POWDERS OF PURE NITROCELLULOSE: POWDER B. *Powder B* was applied in France as a military explosive in 1886, and was used solely as a propellant powder up to the outbreak of the European War. During the war ballistite (*see later*) also was made in France and powder B in Italy, Great Britain and America, the French process being employed; briefly this is as follows: By means of a suitable kneading machine an intimate mixture is made of 66 to 70 parts of guncotton (known in France as CP 1), and 30 to 34 parts of moist collodion-cotton (termed CP 2) (with about 25 to 30 per cent. of moisture). The moisture is not removed by drying in an oven, which would be dangerous, but is displaced by means of 95 per cent. alcohol (Messier process, 1892) in suitable hydraulic presses; each chamber is charged with about 27 kilos (calculated dry) of mixed nitrocellulose, which is supported on a perforated metallic disc on the bottom of the chamber. After the moist cotton has been pressed slightly with the piston, about 18 kilos of alcohol is introduced and forced through the cotton, gradually displacing the water, which is discharged through the apertures at the base and is followed by dilute and then by concentrated alcohol; when the latter issues with its original density, the whole of the water has been displaced. About two-thirds of the alcohol recovered has a concentration of about 50 per cent. and, after direct distillation to separate it from suspended cotton and from part of the water, is rectified to bring it to 95 per cent. strength to be used in succeeding operations (about 5 per cent. of the alcohol is lost in each operation).

The nitrocotton remaining in the press is extracted by means of a counter-piston, which forces it upwards in cakes impregnated with 10 to 11 kilos of alcohol (per 27 kilos of dry nitrocotton). The operation in each chamber occupies five minutes.

These multiple dehydration presses with continuous automatic action produce up to 12 to 15 tons of dehydrated nitrocotton per day, the best form being made by Messrs. Champigneul (Paris).

In some powder B factories, instead of Champigneul presses (which before the war cost about £1600 and during the war as much as £6000), use is made of hydro-extractors, the nitrocotton (40 to 45 kilos) in the moving centrifuge being treated with a spray of 95 per cent. alcohol. Each centrifuge with a perforated drum 1 metre in diameter and a final velocity of 1100 revolutions per minute gives an output of 1600 kilos of dehydrated nitrocotton per twenty-four hours. Almost twice as much alcohol, however, is consumed in the centrifuges as in the presses and the percentage loss is greater; one-half of the alcohol is recovered at about 68 per cent. strength and the rest at 40 to 50 per cent.; the latter is distilled and rectified and the former used for the first treatment in a subsequent operation, being then recovered at 40 to 50 per cent. strength; a second treatment of the nitrocotton with 95 per cent. alcohol yields 68 per cent. alcohol.

Gelatinisation of the nitrocotton is effected most completely and rapidly with a mixture of 66 per cent. of ether and 34 per cent. of alcohol, *i. e.*, 2 vols. of ether and 1 vol. of alcohol (135 kilos of the mixture for 100 kilos of nitrocotton calculated dry), account being taken of the alcohol already present in the nitrocotton. The materials are thoroughly kneaded in a kneading machine, the mass being afterwards discharged into zinc tubs and there left, hermetically sealed, for twenty-four hours for the completion of the gelatinisation.

By means of hydraulic presses similar to those used for food pastes, the pasty mass is converted into strips or ribbons varying from 3 to 6 cm. in width according to the type of powder and about 1mm. in thickness. The ribbons are cut into lengths of about 2 metres, hung on rods and dried in a current of air at 40°, the alcohol and ether being recovered with the help of freezing machines (*see note* on p. 231). The strips, still containing 25 per cent. of solvent, are then cut to the desired width and length (usually 15 to 20 cm.) and afterwards dried on brass gauze for five to six hours at 55° to 60° in a stream of air, from which a little solvent may be recovered.

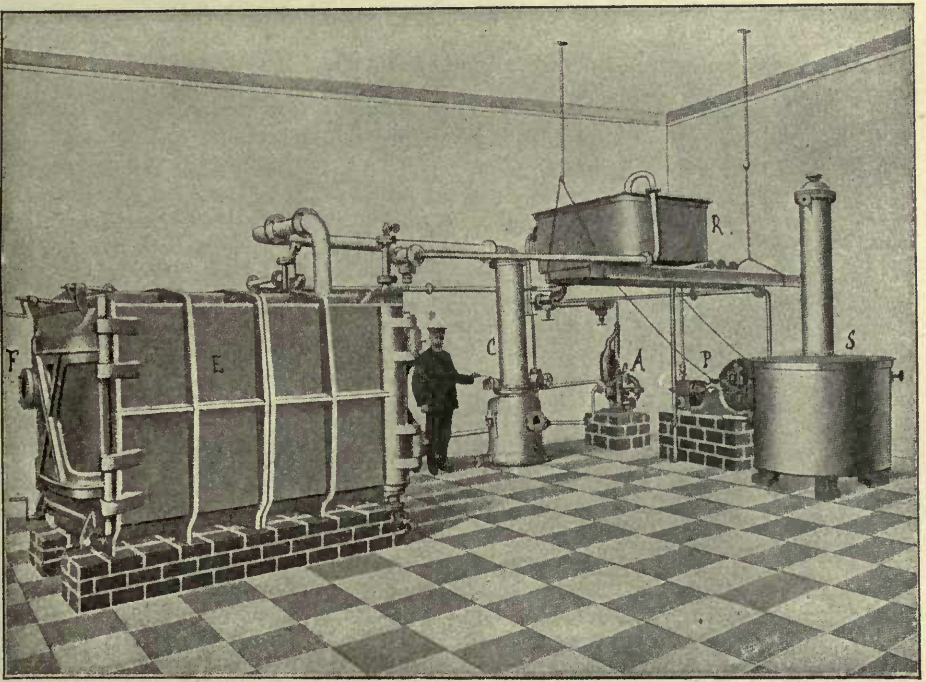

FIG. 209.

In some works this drying is effected under reduced pressure (*see* Fig. 208), special apparatus being used for the recovery of the solvent, as shown in Fig. 209; *P* represents the pump which evacuates the condensation chamber of the solvent *C*, this communicating with the oven *E*. The vapours from the wide tube at the top of the oven are condensed in *C* by means of a bundle of tubes through which water is circulated by the pump *A*. The warm water from the top of the condenser is heated in the coil tank *R* and then circulates in the oven. The condensed solvent is collected in *S* and rectified.

The ribbons, which still contain about 10 per cent. of solvent, are next placed vertically in compact bundles in cases which are immersed for eight or nine hours in vessels of water at 50°. The water discharged from the bath after each operation contains 3 to 4 per cent. of alcohol and is discarded. After draining, the strips are kept in a second drier for some days, until the percentage of solvent (water, alcohol and traces of ether), is reduced to 1·3 to 1·8, and are finally exposed to the air for some days under sheds, thus acquiring a stable composition, which, together with the ballistic effect, remains unchanged even after prolonged storage.

To obtain uniformity in powder B, strips from different operations are well mixed, the mass being translucent and of a pale brownish-yellow colour. Before being despatched it is tested by the ordinary stability tests.

Waste powder B is utilised by softening it with 150 per cent. of alcohol-ether and adding it, little by little, to the mass in the kneading machine.

During the European War, the Angoulême works in France produced about 120,000 kilos of the powder per day, the alcohol and ether consumed amounting to some dozens of tons; the Ferrania factory of the Società Italiana Prodotti Esplodenti had an output of 15,000 kilos per day.

GELATINE DYNAMITES AND SMOKELESS NITROGLYCERINE POWDERS

Gelatine Dynamites, etc. As we have already seen in dealing with the theory of explosives, the explosion of nitroglycerine is accompanied by the liberation of unused oxygen; on the other hand, it is known that guncotton does not contain sufficient oxygen for the complete combustion of the carbon and hydrogen present in the nitrocellulose molecule.

In 1875, A. Nobel conceived the happy idea of associating the two substances by dissolving in nitroglycerine a certain quantity of soluble nitrocellulose, that is, that used in the manufacture of collodion. This procedure gives gelatines of varying consistency according to the quantity of nitrocellulose (collodion-cotton) dissolved. *Blasting gelatine* is made from 90 to 93 per cent. of nitroglycerine and 7 to 10 per cent. of dry collodion-cotton; *gum dynamites,* on the other hand, contain about 97 per cent. of nitroglycerine and 3 per cent. of collodion-cotton, and when they are mixed with about one-third of their weight of absorbent substances (wood-meal, rye-flour, sodium or ammonium nitrate) they form the ordinary modern dynamites, called *gelatine dynamites,* which are still plastic, although less so than the gum dynamites, and are also less violent, and hence serve well for mining purposes. A common type of gelatine contains, for instance, 62·5 per cent. of nitroglycerine, 2·5 per cent. of collodion-cotton, 25·5 per cent. of sodium nitrate, 8·75 per cent. of wood-meal, and 0·75 per cent. of sodium carbonate (which would be best excluded); it has the sp. gr. 1·5, is exploded with a No. 3 fulminate of mercury cap, and is sold in Austria for No. I dynamite, whilst *gelignite* is sold for No. II dynamite and contains 45 to 50 per cent. of gum dynamite and about 50 per cent. of absorbents as above.

At Christiania a non-congealing *gum dynamite* is made from blasting gelatine and a little nitrobenzene and ammonium nitrate; it has a specific gravity of 1·49 and is less effective than the gelatine dynamites.

For military purposes (torpedoes, cannon, etc.), as much as 4 per cent. of camphor is added in Italy, Austria, and Switzerland; these gelatines are thus rendered insensitive and very safe, and they require special detonators (*e. g.,* a mixture of 60 per cent. of nitroglycerine and 40 per cent. of collodion-cotton or compressed guncotton).

In certain commercial products the collodion-cotton is replaced by nitrated wood or straw, while nitrobenzenes, nitrotoluenes (especially liquid dinitrotoluene), etc., are used instead of nitroglycerine.[1]

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[1] It is impossible at the present time to compare the various commercial brands of dynamite of different countries or even of one country, so varied are the types and the ratios of the components, sometimes when the commercial name is the same. Thus No. 1 *ammonia dynamite* (French) contains 40 per cent. of nitroglycerine, 45 per cent. of ammonium nitrate (this, when pure, is not hygroscopic), 5 per cent. of sodium nitrate, and 10 per cent. of wood-meal or wheat-flour; the No. 2 quality of the same brand contains 20 per cent. of nitroglycerine, 75 per cent. of ammonium nitrate, and 5 per cent. of wood-meal. In *Germany,* the name **Gelatine Dynamites** is given to all mixtures prepared from *explosive gum* (96 per cent. nitroglycerine gelatinised with 4 per cent. collodion-cotton) and nitre as absorbent. In *England,* however, No. 2 *gelatine dynamites* are called *gelignites,* and are often formed of 65 per cent. of the gum and 35 per cent. of absorbents (75 per cent. nitre, 24 per cent. *wood-meal*—wood-pulp used for paper, in a dried state—and 1 per cent. of soda). In *Austria, dynamite I* is made from 65·5 per cent. of nitroglycerine, 2·1 per cent. of collodion-cotton, 7·41 per cent. of wood-meal, 24·85 per cent. of nitre, and 0·26 per cent. of soda; *dynamite II* contains 46 per cent. of nitroglycerine, etc., and *dynamite II A,* 38 per cent. of nitroglycerine, etc. In *France,* gelatine dynamites are called *gums,* and are prepared in very varied forms, *e. g., gum M B* with 74 per cent. of nitroglycerine, *gum D* with 69·5 per cent., and *gum E* with 49 per cent.; then there are *dynamite gelatiné* 1, 2*a*, 2*b*, and 2*c* (the last with 43 per cent. of nitroglycerine, etc.), etc. In *Belgium,* gelatine dynamites are called *forcites*; *forcite extra* contains 74 per cent. of nitroglycerine, *superforcite* 64 per cent., *forcite* No. 2 36 per cent., etc.

In *England* the types most commonly used are: *dynamite No. I,* with 75 per cent. of nitro-

Gelatine and gum dynamites have the appearance of plastic masses, the latter, which has the sp. gr. 1·6, being especially horny and translucent. Gum dynamite sometimes exudes a little nitroglycerine and so loses in shattering force; when heated for a long time at 70°, it swells up, becomes spongy and decomposes with formation of red, nitrous vapours; it sometimes ignites in metal boxes when exposed to the sun. It is less sensitive even than dynamite (about six times less) to percussion and special caps of gelatine dynamite are required to explode it. It serves well for use in war, since it is insensitive to discharges, and to render it still less prone to detonation by influence it is mixed with a little camphor. When 20 per cent. of collodion-cotton is dissolved in nitroglycerine, a gum dynamite is obtained which is not exploded by the most powerful caps, and ballistite, which contains 30 to 50 per cent. of collodion-cotton, requires special detonators. After freezing and thawing, it becomes more sensitive and dangerous, as is the case with dynamite. It has a greater shattering power than dynamite and acts better than this under water, which does not wash away the nitroglycerine so easily. Exudation of nitroglycerine occurs more readily than with dynamite and causes some degree of danger. It is used as a basis for the manufacture of smokeless powder. Gelatine dynamite is safer to handle and store than ordinary dynamite, which it is largely replacing.

The *manufacture* of these *gelatinised dynamites* requires collodion-cotton, which is very carefully prepared and is completely soluble in a mixture of alcohol and ether, in addition to which it must possess as great a proportion of nitrogen as possible. When it is not well prepared, although it dissolves in alcohol and ether, it is not readily and entirely soluble in nitroglycerine, or it does not retain the latter completely for a long time. The quality of the collodion-cotton depends, then, on the choice of a good cotton and on exact conditions of nitration—duration, purity of acids, temperature.

This should then be finely subdivided (*pulped*) and dry, so that it can be passed through a fine sieve before being mixed with the nitroglycerine, in which it does not dissolve well if moist. This operation of gelatinisation and kneading is termed in French *pétrinage.* The necessary quantity of nitroglycerine is placed in wide, shallow vessels of copper or lead heated externally by hot water (50° to 60°). After thirty to sixty minutes, when the temperature has reached 45° to 50°, the required amount of dry, powdered collodion-cotton (and the other absorbent substances used for ordinary dynamites, such as cellulose, flour, starch, nitrate, etc.), is added in small quantities and mixed now and then with a wooden spade. It is then left for a couple of hours and afterwards thoroughly mixed by hand, just as dough is mixed, so as to form a homogeneous, soft paste; this, on cooling, forms a more or less hard, elastic, translucent gelatine which constitutes the gelatine or explosive gum. If, instead of collodion-cotton alone, absorbents are also used, *gelatine dynamites* are obtained; these are converted into rolls and cartridges with the machines already described (p. 284). When the gelatine is not intended for the manufacture of

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glycerine; *gelignite* with 65 per cent. of gelatinised nitroglycerine (97 per cent. of nitroglycerine), 25 per cent. potassium nitrate, and 10 per cent. wood-meal; *blasting gelatine* with 93 per cent. of nitroglycerine and 7 per cent. of collodion-cotton; *gelatine dynamite* with 80 per cent. of gelatinised nitroglycerine (with 3 per cent. of collodion-cotton), 15 per cent. of potassium nitrate, and 5 per cent. of wood-meal.

In *Italy* there is *dinamite-gomma A* (or simply *gomma A*, corresponding with the French *gomme extra-forte*) formed from 92 per cent. of nitroglycerine and 8 per cent. of collodion-cotton; *gomma B* (corresponding with the French *gomme à la soude*) with 83 per cent. of nitroglycerine, 5 per cent. of collodion-cotton, 8 per cent. of sodium nitrate, 3·7 per cent. of wood-meal, and 0·3 per cent. of sodium or calcium carbonate or ochre. Commercially, however, the strength is given in terms not of nitroglycerine, but of *gelatine*, that is, the starting material is taken as a gelatine formed by gelatinising 94 per cent. of nitroglycerine with 6 per cent. of collodion-cotton, to which are then added the various absorbents; thus gomma *B* contains 88 per cent. of gelatine (equivalent to 83 per cent. of nitroglycerine). In Italy the old kieselguhr dynamite is no longer used and is replaced by the so-called *gelatine-dinamiti*, which are marked with various letters and numbers; thus *No.* 0, containing 74 per cent. nitroglycerine, 5 per cent. collodion-cotton, 15·5 per cent. sodium nitrate, 5 per cent. wood-meal, and 0·5 per cent. carbonates; *G. D. No.* 1, with 70 to 72 per cent. nitroglycerine, etc.; *G. D. No.* 2, with about 48 per cent. nitroglycerine; and *dinamite No.* 3, with 25 per cent. nitroglycerine, 54 per cent. sodium nitrate, 19 per cent. wood-meal and cellulose, and 2 per cent. soda and yellow ochre. During recent years there have also been prepared in Italy *gelatine-dinamiti*—suggested by Dr. Leroux—with 8 to 10 per cent. of the nitroglycerine (of No. 1) replaced by as much *liquid dinitrotoluene*, which gelatinises cotton well and gives non-congealing dynamites, more economical and almost as powerful as, sometimes more powerful than, the corresponding gelatine-dynamites; these act well in open mines, but give large quantities of unpleasant fumes, and hence are unsuitable for use in galleries, etc.

ballistite (*see later*), the conversion into cartridges is effected by means of an Archimedean screw machine (*boudineuse*), similar to sausage-making machines (Fig. 210).

The *mixing* for causing gelatinisation, especially if other substances besides collodion-cotton are added, may be carried out in mechanical kneading machines (Fig. 211) mounted on a wooden platform, *b*, which can be raised by screws and cog-wheels, *g*, *e*, and *h*, resting on supports, *a a*; on this platform is a double-walled, copper pan, *i j*, which can be surrounded with hot water and can be moved on rollers. Above are the bevel-wheels and pulleys for working the stirrers, *q* and *r*. The nitroglycerine is first heated to 50° by raising the temperature of the water in the jacket of the copper pan, the latter being then raised so as to submerge the stirrers; the ingredients necessary to give the required type of gelatine dynamite are then added. Mixing is complete in an hour. Other forms of kneading machine are also used, *e. g.*, the Werner-Pfleiderer machine, which is employed for smokeless powders and for bread-making. After cooling, the plastic dynamite, which has a yellowish, translucent appearance, is removed from the kneading machine to a separate building to be converted into cartridges. This is done in special machines (*boudineuses*) (Fig. 212 and 213), furnished with endless screws, which force the dynamite or gum from a hole, *B*, in continuous rolls, these being collected in definite lengths in a casing of parchment paper or paraffin waxed paper, *C*.

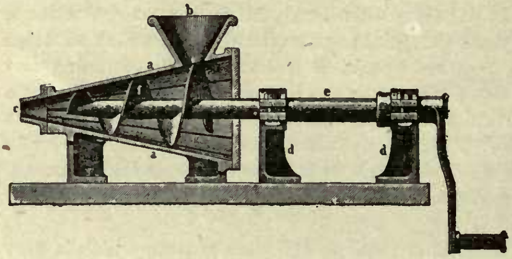

FIG. 210.

B. Military Smokeless Powders. These approach the gum dynamites in character, but contain more collodion-cotton, so that they are safer towards shock and useful as propellants (only slightly shattering).

The most important type is that prepared by Nobel in 1888 under the name of *ballistite* (after he had been preparing since 1878 gum dynamite by gelatinising nitroglycerine with 6 to 10 per cent. of collodion-cotton). *Ballistite* contains about 50 per cent. of nitroglycerine and 50 per cent., or even more, of collodion-cotton (with 11·2 to 11·7 per cent. N). The nitroglycerine for ballistite should be highly stable (for at least twenty minutes at 80° by the Abel test), while the collodion-cotton should have a stability of twenty-five minutes at 71° by the Abel test; for the finished ballistite the stability should reach thirty minutes at 80°. To incorporate these two substances thoroughly and so that there is no danger in the subsequent operations, use is made of Lundholm and Sayer's process, by which the constituents are united in presence of a liquid able to dissolve neither of them. This liquid is merely water, 0·5 to 1 per cent. of aniline or phenylamine, or, as suggested by Spica, phenanthrene, being added to fix the nitrous acids liberated and thus increase the stability of the ballistite.

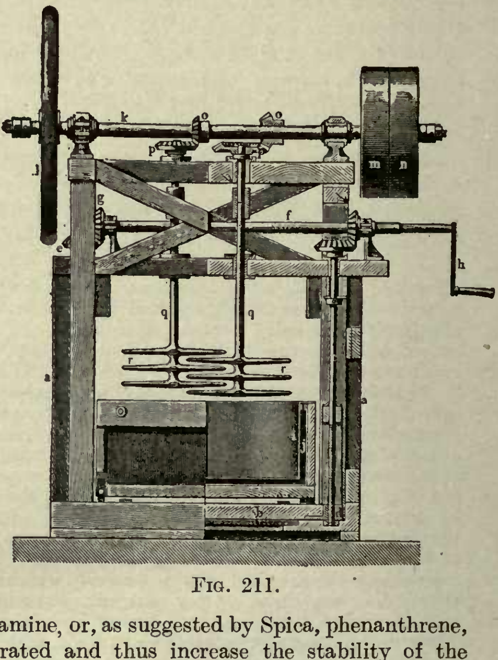

FIG. 211.

The pulped collodion-cotton, containing 30 per cent. of water, as it comes from the centrifuges (after stabilisation with 15 parts of hot water per 1 part of nitrocotton) is introduced into a cylinder of sheet-lead or aluminium containing water at 60°. The mass is well stirred by compressed air and the finely divided nitroglycerine passed in by means of a compressed-air injector. The agitation is continued until all the nitroglycerine is incorporated with the cotton, none remaining suspended in the water. The whole mass in then discharged into a vessel underneath with walls and bottom of fine brass gauze or silk. When it has drained well, the material is removed and left in heaps for some weeks in order that the gelatinisation may be completed. The further treatment consists of coarse sieving, centrifuging to remove non-incorporated water, and a first rolling between two rolls almost touching and heated to about 50 to 60° by means of internal steam (Fig. 214). It is thus obtained in thick non-homogeneous leaves; to the material used to form these leaves are added cuttings and waste of finished ballistite, which is first softened by immersion for some hours in tepid water. The leaves are then rolled a second time between rolls which are more exactly calibrated and adjustable (*see* Fig. 214 *a*), and are heated, thinner sheets of definite thickness being thus obtained. All extraneous bodies (scraps of wood, paper, cotton, etc.) are removed by forceps and the sheets are examined against the light to detect any other heterogeneous particles.

The ballistite is then cut into strips and these into squares, which are seasoned or stabilised by spreading them on cloth under sheds and leaving them for two or three weeks, after which the material undergoes no further change, and is ready to be tested and stored.

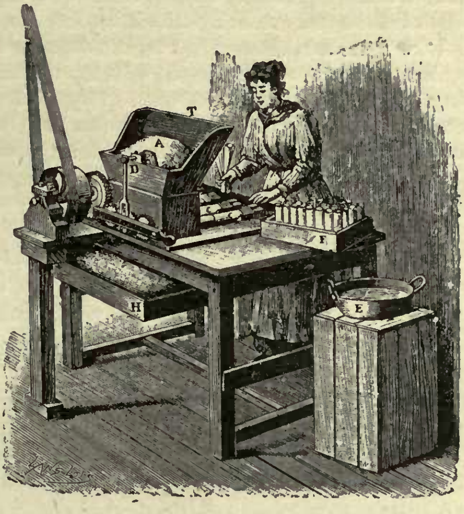

FIG. 212.

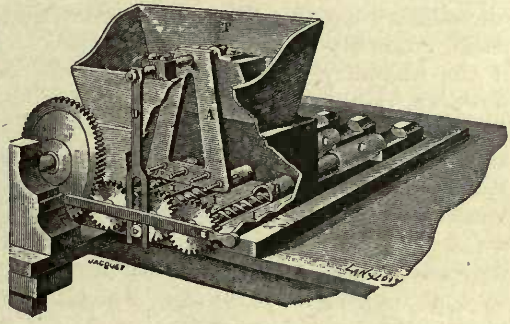

FIG. 213.

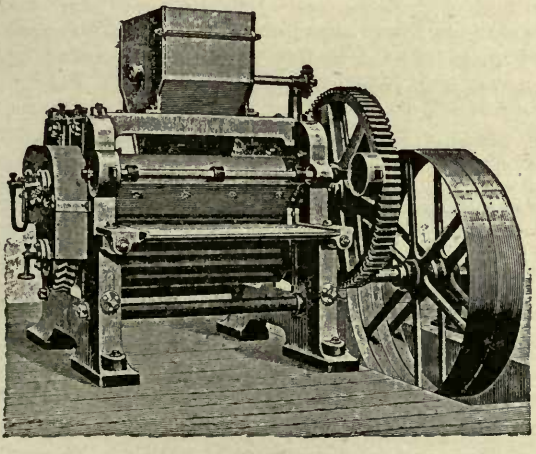

FIG. 214.

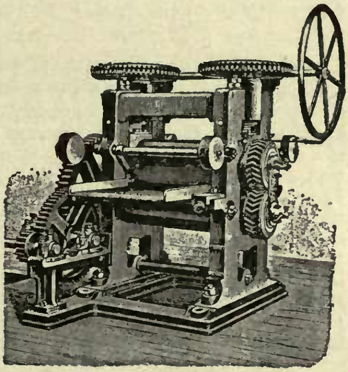

FIG. 214 *a*.

Ballistite is almost brown in colour, has the sp. gr. 1·63 to 1·65, and is practically unaffected by moisture; it inflames at 180° without exploding. The gases formed in its explosion contain no nitrous vapours and do not corrode the firearms to any extent. Such corrosion is caused especially by the very high temperature produced by the explosion of the ballistite and by the friction of the hot gases.

With lapse of time a very small part of the nitroglycerine appears to evaporate, the strength and properties of the ballistite being thereby modified. For this reason ballistite is replaced to some extent by *solenite* and *cordite*, which contain less nitroglycerine.[1]

With some smokeless powders, attempts have been made to replace the nitrocellulose by nitrated starch and the liquid solvents by the corresponding vapours, but no advantage has yet been procured in this way. Explosive gelatines may also be obtained by adding metallic nitrates (of barium or potassium) to the collodion-cotton; these have diminished power but possess the advantage of being readily inflammable. Mixtures of collodion-cotton and nitropentaerythritol have recently been prepared for the use of large-bore artillery.

PROPERTIES OF SMOKELESS POWDERS. Those formed of nitrocellulose alone are hard; ballistite is not so hard, and even in thick strips can be bent and then broken like a very hard paste. They are very resistant to the action of water and so have a great advantage over ordinary black powders, which are destroyed by water. They also possess the advantages of a high density, 1·6 or more (*see* p. 262).

The velocity imparted to the projectile increases with the percentage of nitrogen in the smokeless powder; for one and the same velocity, the explosive which develops the lowest pressure causes the least wear of the barrel and is also the most safe.

Whilst Vieille's smokeless powder (gelatine of pure guncotton) withstands all ordinary conditions of temperature and moisture, ballistite, on the other hand, gradually loses nitroglycerine and so undergoes change of its properties if the humidity of the atmosphere oscillates much. These conditions are, however, rarely met with in practice, and ballistite is used not only by the Italian army and navy, but also by other Governments, and is in some ways superior to the cordite used in the British and also, to a certain extent, in the Italian armies. In 1906, the proportions of the components of cordite were varied slightly and the form altered to that of ribbons, being then known as *axite*. Smokeless powders withstand the blow of a projectile and require special detonators, fulminate of mercury not giving good results. They are exploded by compressed guncotton caps, which in their turn are exploded by fulminate of mercury.

If accidentally ignited, smokeless powders are not very dangerous, since they do not explode, but regard must be paid to the very high temperatures (above 3000°) produced, as these will melt iron, stone, etc.

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[1] *Cordite*, prepared by Abel in 1889, is a smokeless powder in filaments like hollow twine. Modern cordites contain 65 per cent. of *guncotton* (not collodion-cotton), 30 per cent. of nitroglycerine, and sometimes 5 per cent. of vaseline. Guncotton, which is insoluble (to the extent of 90 per cent.) in alcohol, ether, or even nitroglycerine, may also be gelatinised by the action of a common solvent, *e. g.*, acetone, which gives a colloidal solution persisting even after evaporation of the solvent. The dry guncotton is first mixed by hand with nitroglycerine, the mass being then introduced into an ordinary kneading machine, which is of bronze and is jacketed to allow of water-cooling; the acetone (20 kilos per 100 kilos of the paste) is then added and kneading continued for at least 3 hours, after which the vaseline is mixed in for some time. The mass tends to heat and must be cooled. At the end of the operation, lumps of the paste, roughly cylindrical in form, are introduced into the cylinder of the cordite press, which is similar to that used for making macaroni. The threads of varying thickness, length, and shape of cross-section thus obtained are then dried at 40° for five to eight days, and afterwards left for three or four weeks in the air to undergo stabilisation.

Solenite, prepared in a similar manner in thin threads, is used in Italy as a rifle powder, and consists of 36 per cent of nitroglycerine, 61 per cent. of nitrocellulose (one-half guncotton and one-half collodion-cotton), and about 3 per cent. of mineral oil.

Powder C2, made in England by Messrs. Chilworth and also, since 1910, by the Nobel Dynamite Company of Avigliana, resembles cordite, and consists of 70·5 per cent. of nitrocellulose (two-thirds collodion, one-third guncotton), 23·5 per cent. of nitroglycerine, 5 per cent. of vaseline, and 1 per cent. of sodium bicarbonate; gelatinisation is facilitated by the use of acetone.

SMOKELESS AND FLAMELESS EXPLOSIVES. From a military point of view, a great advance was made by the replacement of black powder by smokeless powders, since the latter do not obscure the artilleryman's view and also render difficult the exact location of the battery by the enemy. It still remained possible, however, especially at night-time and with large guns, to determine the position of these, since, as the projectile leaves the muzzle, the hot gases resulting from the explosion extend into the air, producing flames 50 cm. or even a metre in length. A few years prior to the European War successful attempts were made in various countries (Germany, Roumania, etc.) to eliminate these flames almost completely by addition to the explosive of certain substances, especially small proportions of diphenylamine, diphenyldimethylurea, neutral ammonium oxalate, etc. Herein probably lies the reason why the big German guns were able to fire on Dunkirk and Paris from a distance of a hundred kilometres without discovery.

Analogous results are obtained with the so-called safety mine explosives (*see* p. 305).

In 1906 Duttenhofer patented the addition of potassium bicarbonate to smokeless powders to diminish the flame, but the results thus yielded are not highly satisfactory.

Stabilisers for smokeless powders and dynamites. To render these explosives physically more stable, that is, less sensitive to shock, it is sufficient to mix intimately with them paraffin wax, vaseline, camphor (*see* celluloid), mineral oil, castor oil, etc., in more or less large proportions (1 to 10 per cent.).

To stabilise explosives chemically by retarding or preventing their spontaneous decomposition, various additions are made. Thus, after the first cases of such decomposition with powder B, Vieille suggested the addition of a little amyl alcohol (2–4 per cent.), which doubled the stability; in 1896 it was found that a far higher stability still was effected by 2 per cent. of diphenylamine. Aniline, which acts similarly but less efficaciously, has long been added to ballistite. The last stabilisers have the property of fixing any traces of nitrous acid formed during the slow decomposition of the powder, thus preventing rise of temperature and slackening the decomposition. These substances are, of course, sometimes used to mask incipient decomposition at the time the explosives are to be examined.

Of the numerous other stabilisers suggested, the following, which have given good results, may be mentioned: ammonium and sodium ammonium oxalates, urea, nitroguanidine and mercuric chloride (this only masks the reactions by which the stability is controlled).

SHATTERING EXPLOSIVES

AROMATIC NITRO-DERIVATIVES: PICRATES

PICRIC ACID (*melinite, shimose, lyddite, pertite*). As early as the fifteenth century an alchemist obtained an explosive substance by treating a kind of tar with aqua regia, but this acquired no importance in comparison with ordinary gunpowder. The explosive properties of picric acid, $C_6H_2(NO_2)_3OH$, and its salts were studied in the second half of the nineteenth century and assumed considerable importance when, in 1886, Turpin prepared *melinite* from 70 per cent. of picric acid and 30 per cent. of collodion-cotton previously rendered soluble with alcohol and ether; this was regularly used for some years by the French army in place of dynamite. At the present time fused picric acid (m.-pt. 122°; sp. gr. 1·64–1·66) is poured into cartridges containing a fulminate of mercury cap and powdered picric acid. The manufacture of picrc acid from carbolic acid, and also its properties, are described in Part III (chapter in Aromatic Nitro-derivatives).

Weight for weight, picric acid is less effective than dynamite, but, measured by volume, its power is greater than that of dynamite, the specific gravity of which is 1·5. It has also the advantage over dynamite in that it does not freeze, being already in the solid state.

In England, melinite was followed in 1888 by *lyddite*, containing about 87 per cent. of picric acid, 10 per cent. of nitrobenzene, and 3 per cent. of vaseline. This is poured in a molten state into the cartridges and is exploded with ammonium picrate detonators; it is highly resistant to shock. It undergoes decomposition fairly readily, giving poisonous gases, containing about 61 per cent. of carbon monoxide and 13 per cent. of carbon dioxide. For this reason picric acid and all similar compounds cannot be used in the galleries of mines. The ease with which picrates form in contact with iron, lime etc., has led to many disasters, since picrates are readily exploded by shock. The insides of bombs and projectiles to be charged with picric acid are varnished, as also are the capsules for the caps. Fusion of picric acid is carried out in aluminium vessels; at a temperature somewhat above the melting-point, picric acid is highly sensitive and dangerous.

During the European War, in order to increase the quantity of explosive with a basis of picric acid, use was made on an enormous scale of a fused mixture of 60 per cent. of picric acid and 40 per cent. of dinitrophenol (m.-pt. 111·5°; for preparation, *see* Part III). This has explosive powers almost equal to those of picric acid, and is more stable and less dangerous to handle, while it has the great advantage that its melting-point is below 90°, that of picric acid being 122°. Further, for this mixture use may be made of moist picric acid, since the water separates completely and floats on the mass during the fusion; the danger involved in drying the picric acid is thus avoided.

TRINITROTOLUENE. Some years before the European War picric acid had been replaced in Germany, Italy and, partly, in England by trinitrotoluene, which melts at 80·5° and has the same power, but is more stable and less dangerous to make and to handle; further, it does not combine with metals. Part III contains a description of the properties and manufacture of this product, which was used during the war on a vast scale by all the belligerents.

Another explosive which was largely used in the war and is cheap, easily prepared, safe to handle, and moderately powerful, consists of an intimate mixture of 12 per cent. of dinitronaphthalene (a mixture of various isomerides, *see* Part III) and 88 per cent. of ammonium nitrate; the mixture was compressed, but not excessively, in the projectile. This product (and others similar) was patented in 1885 by Favier and in France, during the war, bore the name *schneiderite,* being made at the Creusot works of Messrs. Schneider; in Italy it was made by the Società Italiana Prodotti Esplodenti (S.I.P.E.) of Cengio and was termed *siperite.*

Various other mixtures with bases of atomatic nitro-derivatives (nitrocresols, etc.) were used during the war.

SPRENGEL EXPLOSIVES. In 1871 H. Sprengel, starting from the fact that explosion is nothing but instantaneous combustion, conceived the idea of preparing explosives by mixing a readily combustible substance with one possessing considerable oxidising properties; the substances separately are not explosive, but become so when mixed, mixing taking place only at the spot where the explosive is to be used.

In January 1871, a few months before Sprengel's discovery, Silas R. Devine had prepared and used a mixture of potassium chlorate and nitrobenzene, but he kept the process secret; in 1880 he prepared *rackarock* powder, formed by mixing the potassium chlorate and nitrobenzene just before use (*see below*).

This idea was taken up later by Hellhoff, who mixed nitric acid with nitrated hydrocarbons, and more effectually by Turpin and by R. Pictet, who mixed nitrogen peroxide (N_2O_4) with various nitrated organic compounds and also with CS_2 (*panclastite, fulgurite,* etc.), but these explosives never came into practical use.

Another form of explosive of the Sprengel type is that with ammonium nitrate as base; this has been largely used during recent years and is five or six times as powerful as gunpowder.

The most important of these explosives is *Favier powder* (1885), which, in its different forms, usually consists of a mixture of ammonium nitrate and nitronaphthalenes, and sometimes contains also sodium nitrate, aluminium, etc. (*see later:* Prometheus Powder).

CHLORATE AND PERCHLORATE POWDERS

(Partly of the Sprengel type)

Chlorate powders, first proposed by Berthollet in 1785 to obtain greater power, and containing potassium chlorate instead of nitre, have not been very successful, and even when a part of the nitre is restored, accidental explosions often occur, owing to the great sensitiveness to shock. In America, Devine (1881) retains the potassium chlorate, but keeps the ingredients of the powder separate until required (as is done with the Sprengel explosives (*see above*); thus *rackarock* for blasting contains 79 per cent. of potassium chlorate and 21 per cent. of nitrobenzene (liquid), mixed sometimes with picric acid, sulphur, etc. These powders are rendered less sensitive to shock by mixing with a little wax (*e. g.* Brank's powder). In 1896, at St. Petersburg, Jevler prepared *prometheus* from a solid portion (90 per cent. potassium chlorate + 10 per cent. of manganese dioxide + a little ferric oxide), and a liquid portion (55 per cent. of mononitrobenzene + 18 per cent. of turpentine oil + 27 per cent. of naphtha); a factory for this explosive was erected in Italy in 1905, but it was destroyed by a terrific explosion in 1909, ten persons being wounded and five killed. In 1901 *donnar* was placed on the market; it contains 56 per cent. of chlorate and 24 per cent. of potassium permanganate for the solid part, and 16 per cent. of nitrobenzene and 4 per cent. of turpentine for the liquid part. Also nitronaphthalene and castor oil (5 to 8 per cent.) are used to render the mixture more stable, *e. g.*, with *cheddite* and with *pierrite:* 80 per cent. of chlorate + 12 per cent. nitronaphthalene + 6 per cent. castor oil + 2 per cent. picric acid (or, better, 2 per cent. dinitrotoluene), the whole being well mixed; this powder has double the power of ordinary blasting powder.

To replace dynamite, *miedziankite,* consisting of 90 per cent. of chlorate and 10 per cent. of petroleum, has been suggested (1912).

More advantageous still are thought to be the *potassium perchlorate powders* (*Nisser* powder, 1865, contains: perchlorate, 10·5; nitrate, 44·5; bichromate, 2; ferrocyanide, 1·5; sulphur, 15·5; charcoal, 19·5; and vegetable substances, 6·5 per cent.). Better still are those containing *ammonium perchlorate,* recently invented by U. Alvisi (*manlianite:* 72 per cent. perchlorate, 14·75 charcoal, 13·25 sulphur; *Cannel powder:* 80 per cent. of perchlorate, and 20 per cent. of cannel coal; *cremonite,* with 48·85 per cent. of ammonium perchlorate, and 51·15 per cent. of ammonium picrate; and the *kratites* obtained by mixing perchlorates with nitroglycerine and with nitrocellulose). Perchlorate powders should be used cautiously, and to render them less sensitive without imparing their great shattering power, they are mixed with urea, guanidine, dicyanodiamidine, etc.; if nitrate is added, the chlorine is partly fixed, and the explosions then obtained are especially suited to mines with thin and extended seams. Hydrogen chloride also is formed to some extent in the explosion: $2NH_4ClO_4 = 2HCl + 2N + 3H_2O + 5O$, the theoretical temperature of the explosion being 1084° and the volume of gas liberated 1615 litres of gas per kilo of the explosive.

In 1905 a patent was taken out for a powder containing 47 per cent. of ammonium nitrate, 1 per cent. of charcoal, 30 per cent. of orthonitrotoluene, and 20 per cent. of very finely powdered aluminium, the whole being compressed under a pressure of 5000 kilos per square centimetre, and then moistened with nitrotoluene in a water-bath at 67°.

SAFETY EXPLOSIVES (for Mines Rich in Firedamp).[1] Firedamp (*see* p. 34) is a mixture of methane and air and is formed particularly in coal-mines. It burns at 450° and inflames at 650°; in presence of spongy platinum it burns even at 200°. For ignition to occur, a certain time—at least some seconds—is necessary. For instance, at 650° about 10 seconds elapses before the explosive mixture ignites, whilst at 1000° ignition occurs in 1 second. This explains why, for example, the gases produced at a temperature of 2000° by shattering explosives do not always fire the explosive mixture, the explosion occurring with enormous rapidity (scarcely measurable). The danger of ignition is diminished by decrease of the quantity of gas formed, *i. e.*, of explosive used for each charge; the very hot gases produced expand rapidly and become cooled, so that they are unable to cause ignition of the firedamp. Further, if the heat of the gases is efficiently utilised to give the

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[1] The frequent explosions occurring in mines have led scientific men to make attempts to mitigate their effects and to render them less common. In the tremendous explosion of March 10, 1906, in the Courrière mines (France) there were 1000 victims, 600 being killed; thirteen workmen were rescued alive after twenty days. Commissions have been appointed in France (1880), Russia (1887), Austria (1891), and other countries. In England the question has been studied by Macnab (1876) and Abel (1886); in France by Mallard and Le Chatelier (1883), Watteyne, etc.; in Germany by Winckhaus (1895), very systematically by C. E. Bichel and Mettegang (1904–1907), who devised various ingenious forms of indicating apparatus, Beyling (1903–1907) and Heise (1898); and in Austria by Siersch (1896), Böhm (1886), Mayer (1889), and Hess (1900).

The studies of Bichel more especially have shown that the safety of an explosive for use in mines (especially coal-mines) depends simultaneously on several factors, each of which must lie within definite limits, excess of one of these not being able to compensate for deficiency of another. Thus, for example, ordinary *black powder,* which has almost all the requisites of a safety explosive, cannot be employed, for the sole reason that the duration of its flame is too long and so renders it dangerous. The principal factors establishing the safety of an explosive are: velocity of explosion, temperature of the gases formed, length of the flame, duration of the flame, and quantity of explosive used in each explosion. The results of experiments made in England and America up to 1913 show that the safety of mine explosives is influenced also by the diameter of the cartridge, the density of the charge, the granulation, the tamping, and the degree of moistness of the air.

maximum amount of mechanical work (splitting of the rock), the risk of firing is diminished; hence follows the necessity of a good tamping for each charge in order that the escape of the gases without performing work may be prevented.

Explosion in the open is more likely to ignite firedamp. In mines the use of a powerful detonator is advantageous, in order that the explosion may be sharp and rapid. Mine explosives should contain sufficient oxygen to produce only CO_2 and not the poisonous CO.

Instead of calculating the temperature and duration of explosion, it is preferable in practice to make direct experiments with small cannons placed against a rock at the bottom of a long, wide iron tube or *test-chamber* (20 cu. metres), containing an explosive gas. Discharge of the cannons should not ignite the gas if the explosive is safe. In France it is prescribed by law that in mines explosives must be used which give gases of maximum degree of oxidation but no inflammable gas (CO, H_2) or solid carbide: further, the temperature of detonation, calculated according to a formula of Mallard and Le Chatelier, must not exceed 1500° (or for certain piercing operations, 1900°).

Gunpowder, dynamite, and blasting gelatine readily cause explosion of firedamp in mines, their temperatures of explosion exceeding 2200° (as shown by Mallard and Le Chatelier).[1] In order to meet the requirements of a safety explosive, various ingenious processes are employed to lower the temperature of the gases from the explosion sufficiently to prevent them giving a flame. The charges are wrapped up and the tamping made with water or with gelatine containing 98 per cent. of water (or with special sponges saturated with water, etc.). Salts containing much water of crystallisation have also been used for tamping, but without good results, the tamping being simply projected to a distance without evaporation of the water. A safer plan consists in mixing the explosive directly with such salts, the water of crystallisation then evaporating with considerable absorption of heat, at the instant of explosion. Finally, use is made of explosives with ammonium nitrate as base, the temperature of explosion of the nitrate being only 1130° and the reaction occurring thus: $NH_4NO_3 = N_2 + 2H_2O + O$. Since, however, the explosive effect of ammonium nitrate is small, it is combined with other substances, *e. g.*, with dynamite or with Favier's explosive. In some cases, in addition to the nitrate, ammonium chloride is used, this undergoing dissociation with absorption of heat from the gases.

To lower the temperature of the flame, and especially to obtain smokeless and flameless

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[1] Dynamite and especially gunpowder, if exploded without tamping, will certainly ignite firedamp or even the coal-dust suspended in the air of coal-mines. The danger is diminished, but not excluded, by tamping, so that even in 1853 the Englishman Elliot suggested replacing the explosives by quicklime, a large compressed charge of which is placed in a cavity in the rock; the pipe from a pressure water-pump is then introduced and a good tamping effected. The water, coming into contact with the lime, increases the volume of the latter two to five times, and, with the steam formed at the same time, pressures of 500 atmos. can be obtained. In 1880 the use of lime cartridges was fairly general in mines, but they were abandoned later owing to the unsatisfactory results given. No better fortune befell cartridges of quicklime, water, and sulphuric acid, or powdered aluminium and sulphuric acid (which develop hydrogen), or chlorine and ammonia compressed separately and then united, or compressed explosive mixtures of oxygen and hydrogen. In 1876, Macnab suggested tamping gunpowder charges with water, but this did not always prevent explosion of the firedamp; the same system applied to dynamite by Abel in 1886 gave better results. In some cases, the water is replaced by moist substances (sand, moss, etc.), which yield good results.

In mines which give much coal-dust there is the greatest danger of disaster when large charges (of more than 100 to 150 grams) are used, and when the coal contains 22 to 35 per cent. of volatile products.

Although firedamp ignites at 650°, explosives can be used which have a temperature of explosion only slightly below 2200° (*roburite*, 1616°; *westphalite*, 1806°; *carbonites* for coal-mines, 1820° to 1870°, etc.), since the gases cool on expanding. Even these explosives are, however, dangerous if the charges are large (above 300 grams for roburite and westphalite, and above 1000 grams for the carbonites), since then a momentary pressure on the air is developed (especially if the velocity of explosion is high) and a decided rise of temperature. Explosives which, in charges of 600 to 800 grams, do not ignite the explosive mixture in the test-chamber, may be safely used in fiery mines.

The length and duration of the flame of the explosion are, however, of the greatest importance, and ordinary black powder is, as stated above, very dangerous in such mines owing solely to the marked duration and length of the flame. More dangerous still are those explosives which cause considerable dilatation of the leaden blocks (*see later*, Fig. 230, p. 317), and those which give, among their products of explosion, carbon monoxide and hydrogen, but not oxygen, since these gases on burning (rapidly) withdraw oxygen from the flame of the explosive and almost stifle it. A good safety explosive ceases to be such if it is not always prepared with the same care and of equal uniformity from the same materials.

powders, addition of nitrodicyanodiamidine or dicyanodiamide (*see* Vol. I., p. 371) has been tried with success. Use has also been made of vaseline, oil of paraffin, camphor or 2 to 5 per cent. of sodium oxalate, tartrate, or citrate (Ger. Pat. 243,846).

Various kinds of such explosives give good results, *e. g.*, *grisounite*, containing 44 per cent. nitroglycerine, 12 per cent. nitrocellulose, and 44 per cent. crystallised magnesium sulphate ($MgSO_4 + 7H_2O$); also *roburite*, with 82 per cent. of ammonium nitrate and 18 per cent. of dinitrobenzene; Nobel's *wetter-dynamite*, with 53 per cent. nitroglycerine, 14·3 per cent. kieselguhr, and 32·7 per cent. magnesium sulphate; *securite*, with 37 per cent. ammonium nitrate, 34 per cent. potassium nitrate, and 29 per cent. nitrobenzene; *westphalite*, containing 94 per cent. ammonium nitrate, and 6 per cent. resin; *carbonite*, with 25 per cent. nitroglycerine, 40 per cent. wood-meal, 30·5 per cent. potassium nitrate, 4 per cent. barium nitrate, and 0·5 per cent. sodium carbonate; *ammoncarbonite* contains 82 per cent. of ammonium nitrate, 10 per cent. of potassium nitrate, 4 per cent. of nitroglycerine, and 4 per cent. of wheat flour; *vigorite*, containing 30 per cent. nitroglycerine, 49 per cent. potassium chlorate, 7 per cent. potassium nitrate, 9 per cent. wood-pulp, and 5 per cent. magnesium carbonate. Even these substances are not, however, safe in the absolute sense of the word; with such additions of inert products, the explosives lose in force but gain in safety.

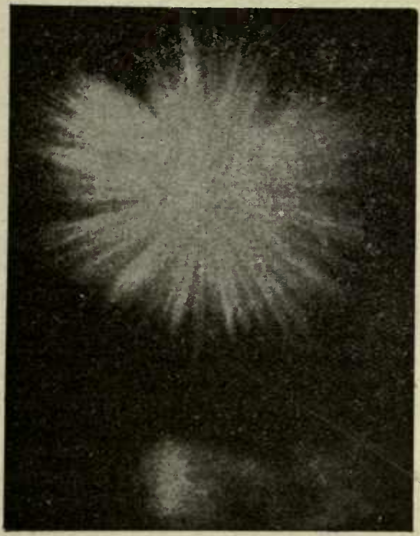

FIG. 215.
100 grams of Gelatine Dynamite

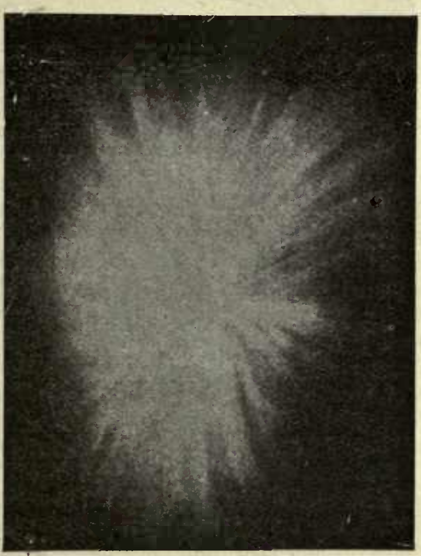

FIG. 216.
100 grams of Dynamite (Kieselguhr)

FIG. 217.
100 grams Roburite

FIG. 218.
100 grams Carbonite

FIG. 219.
100 grams Grisounite

In 1896 Schöneweg, and then Siersch, starting from the hypothesis that the smaller the flame produced in an explosion, the safer will be the explosive, photographed, on dark nights, the flames produced by the free explosion of 100-gram cartridges. As will be seen from Figs. 215 to 220, these flames are of value, although they are not absolutely decisive, since the non-luminous (ultra-violet) rays also act on the photographic plate. In Fig. 215 is seen a small luminous spot detached from the principal flame, this being due either to the surrounding gas being rendered incandescent by the shock of the explosion, or to subsequent inflaming of the gases of the explosion.

FIG. 220.
100 grams Gelatine Dynamite, with tamping of wet paper

DETONATORS AND CAPS

FULMINATE OF MERCURY, $(C:N\cdot O)_2Hg$, the composition and constitution of which are given later (*see* Fulminic Acid), was discovered by Howard in 1799, and studied as regards its constitution by Gay-Lussac, Liebig, Gerhardt, Kekulé, etc. The first mercury fulminate cap was made in 1815 by Durs Egg. Its manufacture requires great care and exact proportions of the reagents. So long as fulminate of mercury is moist it presents no danger, but it must be handled with extreme care when dry.

It is best prepared by Chandelon's process: into a glass vessel of about 4 litres capacity is placed 100 grams of mercury, to which is added 1000 grams of nitric acid of 40° Bé. (sp. gr. 1·383), the liquid being stirred until all the mercury is dissolved. The greenish liquid is allowed to cool to about 20° and is then poured into a flask of at least 5 litres capacity containing 635 grams of 90 per cent. alcohol; bumping or fuming of the liquid is of no consequence. Very soon the liquid begins to boil spontaneously, to become decolorised and to evolve gas and white poisonous vapours (CO, ethyl nitrate and acetate), and then yellow vapours of nitrogen peroxide.

The mass darkens slightly, and when the maximum fuming occurs, 80 grams of 90 per cent. alcohol are added a little at a time, and then a further quantity of 55 grams of alcohol, the boiling being thus somewhat attenuated. After it has been left until the white vapours have disappeared, there appears on the bottom a voluminous whitish powder, which is the fulminate of mercury. The operation lasts altogether fifteen to twenty minutes, and should be carried out under a hood with a strong draught, or else the flask should be fitted with a stopper and wide delivery tube to carry the vapours to a flue. The product is poured on to a filter, washed ten to fifteen times with water—until the wash-water no longer shows an acid reaction [1]—and the filter with the fulminate spread out on other absorbent paper in the air (not in the sun) until it is almost dry (about 20 per cent. of moisture being left, since then it may be kept safely in cardboard boxes). To dry it completely and safely, vacuum drying-ovens at a temperature below 40° are now used.

The reaction between alcohol and mercuric nitrate begins only in presence (that is, after the formation) of nitric oxide, the alcohol being then converted into aldehyde; indeed, if the alcohol is replaced by acetaldehyde the reaction proceeds better and more completely (Munroe, 1912).

Theoretically 100 grams of mercury should yield 142 grams of the fulminate, but practically about 125 to 128 grams are obtained. The preparation of 1 kilo of fulminate requires 8 kilos of alcohol, which is only partially recovered by passing all the vapour emitted during the reaction into a vessel of water. In the dry state, it is sold at 9*s.* 6*d.* to 12*s.* per kilo; when not used at once, it is stored under water. If necessary, it may be purified by dissolving in hot water (solubility 1 : 130), from which it crystallises on cooling. It is whitish or sometimes faintly yellow (if a small quantity of HCl or NaCl is added to the nitric acid used in its manufacture, white crystals are obtained), poisonous and soluble in alcohol.[2]

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[1] The filtrate and the wash-water are utilised by first neutralising with milk of lime or calcium sulphide (or by decomposing with hydrochloric acid); from the precipitate the mercury is recovered, whilst witherite is added to the liquid to form barium nitrate; the alcohol is recovered by distillation.

[2] **Analysis of Fulminate of Mercury** (Brownsdon's method): the fulminate is first purified by dissolving it in potassium cyanide and reprecipitating it with dilute nitric acid; it is filtered, carefully dried, and a weighed quantity of 0·04 to 0·05 gram dissolved in 30 c.c. of water. One gram of thiosulphate is then added and the liquid shaken and made up to 100 c.c. with water. The free alkali in 25 c.c. of this solution is then estimated by titration with N/10-sulphuric acid in presence of methyl orange as indicator.

It has an extraordinary shattering power owing to its very great rapidity of explosion. It is exploded by a blow or by brisk rubbing, and gives a pressure of 27,400 atmos. When heated slowly it explodes at 152°. All objects used in its manipulation must be of wood, not of iron. Since it is scarcely ever used alone for preparing caps, but is mixed with 15 to 20 per cent. of potassium chlorate and about 25 per cent. of antimony sulphide, it is sometimes, in order to avoid explosion, made into a paste with a thick solution of gum, the required quantity being poured into each copper cap (which contains about 15 or 20 mgs. of fulminate for sporting caps, or 1 to 1·5 grams for caps to be used with dynamite cartridges), these being then very carefully dried in vacuum drying ovens. When, however, these mixtures are prepared in the dry state, in order to prevent explosion the mixing is carried out in the apparatus shown in Figs. 221 and 222. In a leather box, *e*, a leather bag, *f* (the so-called "jelly-bag"), is suspended by the loops, *h*, attached to the gutta-percha ring, *g*. To the bottom of the bag and to the ring, *g*, are joined several cords on which are threaded rubber rings, alternately large and small. Another cord, *n*, attached to the lever, *p q s*, admits of the bottom of the bag being raised and lowered so as to mix the ingredients. When mixing is complete the bottom of the bag is drawn completely up, so that the contents fall into the space between the bag and the box and thence into the collecting vessel, *v*.

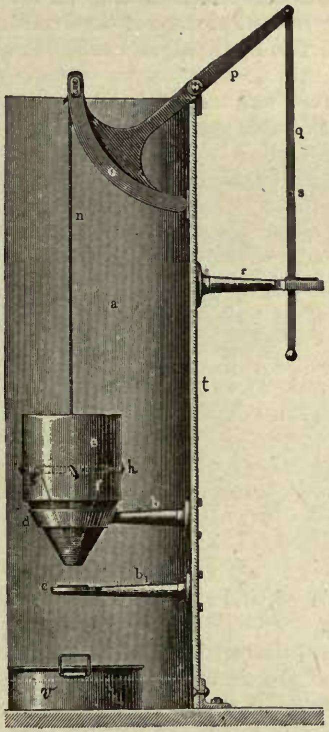

Fig. 221.

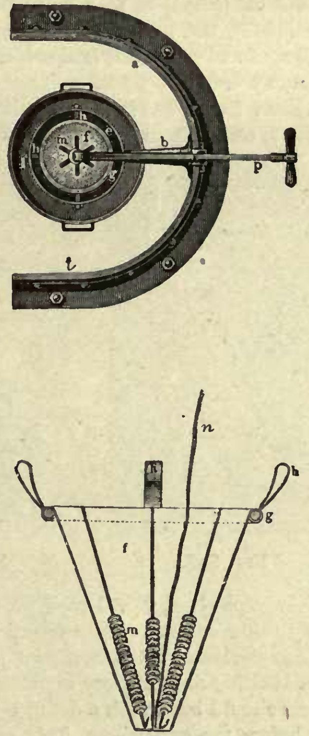

Fig. 222.

The workman is protected from the effects of a possible explosion during the operation by a semi-cylindrical wrought-iron screen, *t*. The caps are then very carefully charged by compressing the mixture with a suitable machine or press, which gives a pressure rising gradually to 260 atmos. (pure fulminate will stand 7000 atmos. without exploding, but in presence of other substances, *e. g.*, sand or coke powder, or other hard body, it will explode with a very small pressure). During the charging the operative is always sheltered by iron screens.

DETONATORS (Caps, Fuses). Detonators serve to produce explosion of explosive substances. For black powders it is sufficient to produce a spark in the mass by means of a heated fuse, but with nitroglycerine or guncotton explosives, neither the fuse nor the black powder causes explosion, ignition being the most they produce. In these cases use is made of fulminate of mercury caps, which explode by simple percussion or heat, and produce a true explosive wave capable of inducing the instantaneous decomposition, *i. e.*, the explosion even of large masses of explosive, provided that the cap is of suitable size; if, however, too little fulminate is used, part of the charge does not explode. Moist or paraffined compressed guncotton requires more powerful caps of dry guncotton, these being then exploded by fulminate of mercury detonators.

Ignition caps, unlike *detonating caps*, contain also a little potassium chlorate.

Smokeless powders require ignition caps with a very hot flame, which is obtained by adding to the fulminate a combustible substance or, as proposed by Brownsdon and the King's Norton Metal Company, a little powdered aluminium.

In 1900 Bielefeld found that it suffices to place a small quantity of mercury fulminate on trinitrotoluene or other aromatic nitro-derivative to obtain an excellent detonator, and in Germany a large proportion of the caps have a basis of trinitrotoluene. *Tetranitromethylaniline* (*tetryl*) is also manufactured as a detonator. According to Wöhler and Matter (1907), the fulminate may be replaced by a small amount of silver azide, and in 1908 Hyronimus suggested *lead azide*, $Pb(N_3)_2$ (*see* Vol. I., p. 376) as a substitute, but this is not always advantageous.

Whereas formerly, for kieselguhr dynamite, use was commonly made of fulminate caps No. 3, and only in exceptional cases of No. 5 (double strength), nowadays, especially for safety explosives, No. 6 caps are mostly employed, and sometimes No. 8 (2 grams of mercury fulminate) to obtain complete explosion.

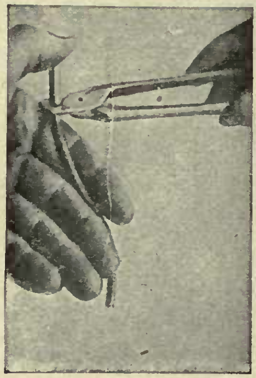

FIG. 223.

FIG. 224.

FIG. 225.

The explosion of detonators or caps, and hence of the cartridges or charges of explosive, both in blasting and military operations, is effected electrically or with *fuses*.

Fuses should burn with a definite velocity, so as to allow the miners to reach a place of safety before the explosion. This requirement is satisfied by the *Bickford fuses* (devised in 1831 by the Englishman, Bickford). These consist of a compact cord prepared in a special manner from jute or cotton threads, which are spun round one another in opposite directions and are rendered impermeable by tar or gutta-percha. These fuses or cords, 5 mm. thick, have an empty central core, which is then filled with finely granulated, compressed powder. They then burn with a velocity of 1 metre in ninety seconds. To explode black powder, it is sufficient to fix the fuse into the mass of the charge, which explodes as soon as the flame reaches it.

These Bickford fuses became of practical importance only in 1867, when the use of dynamite in mines commenced.

For dynamite, gelatine dynamite, and explosive gums or gelatines, use is made of a fulminate of mercury detonator which explodes a dynamite cartridge, this then causing explosion of all the other cartridges (without caps) surrounding it. The fuse is cut clean and introduced into the bottom of the copper cap containing the fulminate, and is fixed to the cap by squeezing it with suitable pincers (Fig. 223). The parchment paper at one extremity of the cartridge is then opened and the cap thrust into the cavity left for it (Fig. 224), the paper being then tied tightly round the fuse with string so that the cap and fuse cannot become detached from the cartridge (Fig. 225).

Ordinary fuses, which are very irregular, are obtained by soaking soft cotton cord with lead or potassium nitrate; such fuses must be well dried before use, as they are hygroscopic. The cord may also be impregnated with a paste of gum and fine black powder and then dried. Almost instantaneous fuses may be made from guncotton.

The importance of tamping after the introduction of the cap into the charge has already been mentioned; if the explosion is carried out in the open, the charge is covered with earth or stones.

Electric fuses are used, especially for dynamite and fulminate caps, and serve well for producing the simultaneous explosion of several charges, this giving a greater effect than separate explosions; they are also useful in galleries which contain firedamp, as the latter would be exploded by a burning fuse. A spiral of thin platinum wire is fixed in contact with a little dry guncotton above the fulminate of the cap. The two ends of the wire are connected separately with two insulated wires joined to a small battery, accumulator, or hand dynamo, which heats the wire and so causes explosion. Use is often conveniently (since the fragile platinum spiral is eliminated) made of an electric spark formed between two platinum points very near to one another in a mixture of potassium chlorate and antimony sulphide contained in the cap; in this case the sparking is effected by a device similar to a Leyden jar (*Bornhardt exploder*) which gives a high-tension current, or by one utilising induced currents (*Bréguet exploder*); these may be placed at a distance from the charge by lengthening the conducting wires.

At one time ignition was effected by means of a high tension current from a frictional machine, Bréguet alone using low tension current, but the tendency nowadays is to employ the latter, together with magnetic ignition, the danger of igniting the inflammable gases of mines being thus diminished. Formerly, very long conducting wires could not be used owing to the weakening of the current at the igniting extremities, but nowadays *relays* are inserted at various points and maintain the current constant.

Lauer and Tirmann make friction igniters, which are operated at a distance by means of wires.

Girard obtains detonating fuses by filling leaden tubes with nitrohydrocellulose and then drawing them out to the diameter of ordinary safety fuses. Similar fuses were made subsequently to 1906 with fillings of melinite or, better, trinitrotoluene.

The best of these fuses are those with instantaneous ignition proposed by General Hess and used in the Austro-Hungarian Army: these were first formed of four threads covered with fulminate of mercury, but in 1903 Hess rendered their action slower by adding 20 per cent. of hard paraffin wax to the fulminate.

When knotted, these *instantaneous fuses* behave as detonating caps and electric ignition may be dispensed with; they may be cut and beaten without danger.

With *detonating fuses* (1910) containing compressed powdered explosive with a detonating velocity of 5000 metres per second (picric acid or trinitrotoluene), the wick is bent and the bend fixed into the cap, whilst the two ends are brought near to the outside and ignite simultaneously. Where the explosive waves meet the shock is such that the waves reinforce one another, producing a velocity of detonation of 10,000 metres per second; in this way the charge is more completely exploded.

VARIOUS POWDERS. During recent years there has been very keen rivalry between different makers to prepare new powders for special purposes (even for shooting pigeons !), and also blasting powders more economical than black powder. For powders to be used immediately or stored in very dry magazines, the potassium nitrate is replaced by *sodium nitrate* (although this is more hygroscopic), which is cheaper and gives a larger proportion of oxygen; the charcoal has also been partially replaced by other organic substances (tar, sawdust, flour, and even horsedung). These powders, often short-lived, are given most extravagant names (*violette*, *gunn*, *fulöpite*, *pyrolite*, *pudrolite*, etc.).

Normanite is an English powder for use in mine galleries, and is composed of 33 per cent. nitroglycerine, 45 per cent. KNO_3, 1·5 per cent. of collodion-cotton, 8 per cent. of wood-meal, 11 per cent. of ammonium oxalate, and 1·5 per cent. of wood charcoal. *Faversham* contains 80 to 90 per cent. of ammonium nitrate, 9 to 11 per cent. of T.N.T., and various other products.

Rexite contains 7·5 per cent. of nitroglycerine, 66 per cent. of ammonium nitrate, 14 per cent. of sodium nitrate, 7·5 per cent. of T.N.T., 4 per cent. of wood-meal, and less than 1 per cent. of moisture. *Ammonal*, which was used as a shattering explosive during the

European War, was employed first in mines, and contains 3 per cent. of coarsely powdered aluminium, 4 per cent. of T.N.T., and 93 per cent. of ammonium nitrate. It was proposed by Escales and Dekman in 1899–1900, and burns slowly, exploding only with powerful caps. Other special types of dynamite are mentioned on p. 284.

DESTRUCTION OF EXPLOSIVES. In various cases it is necessary to destroy explosives, when these have altered or undergone partial decomposition, or when residues are left from samples submitted for analysis. With black powder it is sufficient to immerse it in water and so dissolve out all the nitre, and then to burn the barely dry insoluble residue. Water does not, however, destroy nitroglycerine or the various dynamites; with these the caps are carefully removed and also the wrapper (including the parchment paper), the cartridges being placed in contact one with the other on a long strip of paper in a field free from stones and away from any building; they are then sprinkled with petroleum, and a long fuse, attached to the first cartridge, lighted. In this way the cartridges burn without exploding. With frozen dynamite cartridges which have undergone change, it is dangerous to handle them, and they must be very carefully exploded one by one in the open with a fulminate cap and fuse. Nitroglycerine may be made into a paste with sawdust and burnt as described above. Small quantities of explosives may be burnt in pieces the size of a pea, and small dynamite residues may be decomposed by heating on a water-bath and frequently stirring with concentrated alcoholic caustic soda solution.

STORAGE AND CARRIAGE OF EXPLOSIVES. Explosives factories are placed at a distance of about 1000 metres from any dwelling-house or frequented street. The ideas underlying the construction of magazines are very varied. In some countries (Austria, Italy, France, and, in part, Germany) the prepared explosives are distributed in a number of small magazines far from the factory, and constructed of wood so as to minimise the danger from projection in case of explosion; they are separated by large mounds of earth as high as the magazine, so that the explosive wave or projected material may not reach neighbouring magazines. Also in some magazines a kind of wide bridge covered with earth is constructed over the magazine to annul or attenuate the effect of projectiles falling from above. In England, however, it is assumed that, owing to the perfection of the systems of manufacture and of chemical and physical control of explosives, explosion is not to be regarded as possible, so that large, very solid magazines are built, either wholly of cement or partly of iron, the walls being half a metre thick. The distance between the separate magazines varies from 100 to 200 metres, according as the amount of explosives stored is more than 2000 or 10,000 kilos. The flooring is of wood, and the magazines are heated in winter by means of steam-pipes in order to prevent freezing of the explosives. In general there are no windows, but only double doors and small apertures; artificial illumination, which is rarely used, consists of lamps placed outside the apertures or electric lamps hermetically sealed with gutta-percha and fitted with several glass coverings; in some cases the electric lamps are immersed in water.

Any person entering a magazine must wear felt slippers or leather boots without nails. The most serious danger is not that of accidental explosion, but that of lightning. When storms threaten all work is suspended, while the magazines are protected from lightning by all the most modern appliances.[1] Even the methods of packing explosives and loading

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[1] In general the protection afforded by lightning conductors is due to the fact that lightning is rendered harmless if it meets good and sufficiently extensive conductors of electricity. There is, however, always great danger if inside or outside the buildings protected there are large masses of good conducting materials, such as the iron and lead pipes of dynamite factories, as these may cause deflection of the lightning even from its path in the lightning conductors.

At the Nobel dynamite factory at Krümmel, on the Elbe, there was a great explosion in 1900, lightning striking the iron compressed-air pipe and being thus led to the vessels full of nitroglycerine, which consequently exploded.

Franklin's principle, according to which a metal rod furnished with points should serve to discharge to earth the large electric charges of the clouds, is not applicable to the protection of explosive factories, since such rods on factories do not discharge the clouds to a sensible extent, but can only serve to conduct the lightning to earth after the shock. Much more rational is Faraday's method of attempting to discharge the electricity of the clouds or to conduct the lightning by so many metallic wires as to prevent it from subdividing, no secondary circuits which might produce sparks being, however, formed. According to Faraday, the most certain protection against lightning consists of a metal cage surrounding or covering the building to be protected, and many military explosives stores are effectually protected in this manner. In 1900, Professor Weber proposed the protection of the Krümmel explosives factory by fixing to them on wagons for transport are subject to detailed regulations: by legislation dating from 1875 in England and from 1905 and 1909 in Germany, and in Italy by a series of laws and regulations of various dates. In every case, a despatch must be preceded by a permit and by a warning to all the stations on the route. Explosives are despatched only on certain days and in certain trains. In Germany, chlorate and perchlorate travel without restrictions. Owing to the great stability of modern explosives, only 6 out of 265 accidents due to explosives occurred during transport.

ANALYSIS OF EXPLOSIVES. The quantitative determination of the components of black powder is comparatively simple: 10 to 20 grams of the sample is dried in an oven until constant weight (*moisture*) and is then extracted with hot water, which dissolves the *nitre*, this being weighed or analysed separately. From the dried residue the *sulphur* is extracted by carbon disulphide in a Soxhlet extraction apparatus. The residue then contains the charcoal, graphite, and any impurities (sawdust, mineral carbon, etc.) which may be identified under the microscope. The density of the powder is determined by means of a *densimeter*, and the size of the grains and the quantity of dust by suitable sieves.

The *analysis of dynamites* and of smokeless powders is more complicated and must be carried out with great care. In *dynamites with inert bases* the proportions of nitroglycerine, moisture, and inert substance are determined: 8 to 10 grams of the dynamite, cut into pieces the size of peas, with a wooden or bone spatula, are weighed on a clock-glass and left in a desiccator over calcium chloride (not sulphuric acid) for some days until of constant weight: the loss in weight gives the *moisture*. The dried mass is extracted with pure dry ether free from alcohol, in a Soxhlet apparatus (as in the extraction of fat, *which see*), the heating being effected with water at 50° to 60° and the ether subsequently distilled with water at 40° to 50° away from the neighbourhood of a flame. The nitroglycerine becomes turbid when almost all the ether is evaporated, but clear again when the evaporation is complete; the *nitroglycerine* is dried until constant in weight in a vacuum desiccator over calcium chloride. The residue left in the extractor (*kieselguhr* or other inert matter) is dried at 60° to 70° and weighed. It is sometimes sufficient to determine the nitroglycerine by difference from the weight of this residue; the result is exact enough and the operation more rapid and less dangerous.

Dynamites with *active bases* sometimes have complex compositions and the analysis is not always so easy;[1] in general, the nitroglycerine and collodion-cotton are separated

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iron columns galvanised wire-netting (88 meshes per sq. metre) furnished with metal points so as to form a kind of roof a metre or more above the factory.

The columns also are provided at the top with metal points and serve to conduct the electric discharge to the earth. In the wires forming the network sharp curves are avoided in order to facilitate conduction and hinder any divergence of the lightning. Above the buildings of the Krümmel factory there are 24,000 metres of metal wire with five million points, which may contribute in some measure to discharge the clouds, and would certainly conduct the lightning to earth after a discharge. The ideal method would consist in using copper wire 1 cm. in diameter, but the expense of this would be enormous. The earth-contact is made in wet places with iron plates or rails one or two metres under the soil. Also the metal piping (if not replaceable by rubber tubing) and apparatus of the various parts of the factory are connected with the earth-conductors of the lightning conductors, so as to avoid the formation of sparks in the discharge of the lightning.

It has also been suggested that, where possible, the large vessels in the separate buildings should be electrically insulated, both from the lightning conductors and from the earth.

[1] For *dynamites with active bases* (containing nitroglycerine, collodion-cotton or guncotton, nitrates, sawdust, etc.), Stillman and Austin (1906) propose a method of analysis which is briefly as follows: The moisture is determined on 10 grams as above; the dry mass is then extracted several times in the cold with a mixture of 1 part of alcohol and 2 parts of ether. The residue (*A*) is dried and weighed (for its analysis *see later*), the solution being left to evaporate in the cold to 100 c.c., to which is added 100 c.c. of chloroform to precipitate the collodion-cotton. The liquid is decanted on to a tared, dry, cloth filter on to which all the *collodion-cotton* is brought by means of chloroform; the filter is dried in an oven at 40° and then in a desiccator and weighed (as a check, it is redissolved in alcohol and ether, reprecipitated with chloroform, collected on a filter and dried at 40°, the collodion being then detached from the filter, completely dried on a watch-glass in a desiccator and weighed). After the collodion-cotton is separated, the decanted and filtered liquids are evaporated in a tared vessel, dried in a vacuum and the remaining *nitroglycerine* weighed.

If the nitroglycerine contains traces of *nitrates*, these are extracted by repeated treatment with small quantities of water, the solution being then evaporated and the nitrates weighed. If along with the nitroglycerine there are also resin, paraffin wax, and traces of sulphur, it is titrated with excess of normal alcoholic caustic soda in the hot, the excess of alkali being then from the residue by alcohol and ether, from which the collodion-cotton is precipitated with chloroform.

The resistance to heat of nitroglycerine and of dynamite is determined as with nitrocellulose (*see below*), the nitroglycerine being extracted from dynamite by displacement with water, and the gelatine explosives being mixed with double their weight of chalk prior to extraction with solvents; it should withstand a temperature of 70° for at least fifteen minutes without colouring starch and potassium iodide paper. In contact with sensitive blue litmus paper it should not give the slightest reddening, as this would indicate incipient decomposition.

Exudation of nitroglycerine from dynamite, in either the cold or the hot, shows faulty manufacture.

With *nitrocellulose*, besides testing its solubility in a mixture of 1 part of alcohol and 2 parts of ether which dissolves collodion-cotton but not guncotton, the nitrogen is often estimated in the Lunge nitrometer (Vol. I., p. 578) by shaking with concentrated sulphuric acid; or Schlösing's method, as used in France, may be employed to ascertain the type of the nitrocellulose: in a 150 c.c. flask are placed 25 grams of pure, powdered, ferrous sulphate, 0·7 to 0·8 gram of nitrocellulose, and 70 to 80 c.c. of hydrochloric acid; the flask is shaken and then fitted with a stopper through which pass a delivery-tube and another tube conveying a current of carbon dioxide; when all the air is expelled the delivery-tube, dipping into a vessel of mercury, is covered with a graduated tube filled half with mercury and half with caustic soda solution. The flask is then heated to boiling, when the liquid blackens and in ten minutes all the nitric oxide is evolved, the last traces of this gas being driven out by a stream of carbon dioxide. The volume of gas gives the amount of nitrogen.

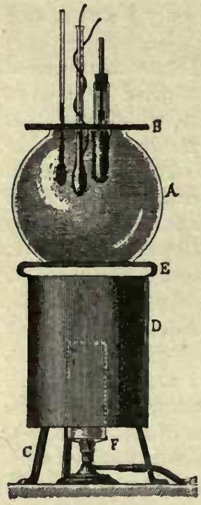

Fig. 226.

The amount of non-nitrated cotton is determined by boiling 5 grams of the substance with a saturated solution of sodium sulphide, the liquid being decanted after a stand of twenty-four hours and the treatment with sodium sulphide repeated; the residue is finally collected on a tared cloth filter, washed with boiling water, then with dilute hydrochloric acid, and lastly with boiling water again; it is then dried and weighed.

The *resistance to heat* (*Abel's heat test*) of nitrocellulose is of importance, as it serves as a control during manufacture and is used also as a test for nitroglycerine: a wide-mouthed glass flask, *A* (Fig. 226), 20 cm. in diameter, and with no neck, is almost filled with water and is covered with a leather disc pierced by four holes provided with wire clips for holding test-tubes; the flask is heated below by a small lamp, *F*, placed under a metal gauze and

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determined with normal acid in presence of phenolphthalein: 1 c.c. of normal alkali used in the saponification corresponds with 0·0757 gram of *nitroglycerine* (in case no resin is present). After the titration, the liquid is evaporated almost to dryness to eliminate the alcohol, and is then diluted with water and shaken with ether in a separating funnel.

The ethereal solution is separated and evaporated, and the residual paraffin wax weighed. The aqueous liquid after separation of the ethereal solution, is heated with a little bromine to oxidise the sulphur; it is then acidified with HCl, boiled, and the *resin* collected on a tared filter, whilst in the filtrate the sulphuric acid formed by oxidation of the *sulphur* is precipitated with $BaCl_2$.

The nitroglycerine may be estimated by difference, by subtracting from the original weight the insoluble residue, *A*, the paraffin wax, the resin, the small amount of sulphur, and the nitrates.

The residue, *A*, insoluble in alcohol and ether (*see above*), is extracted with hot water; the undissolved part is dried at 70° and weighed (B = sawdust + sulphur + any insoluble mineral substances); the *sulphur* is extracted with carbon disulphide, and weighed, this weight subtracted from *B* giving the *sawdust*, from which also the weight of ash left after calcining is subtracted if inorganic substances are present.

The aqueous solution obtained from *A* is evaporated, dried at 110° and weighed (C = nitrates + carbonates + any woody extract); it is then treated with a little nitric acid, evaporated, dried and weighed (*D*); from the difference between *C* and *D* the CO_2 evolved and hence the carbonates can be calculated.

The mass, *D*, is melted, heated to redness, cooled, treated with a little dilute nitric acid, evaporated, dried at 110° and weighed (*E*); this weight gives the sodium and potassium nitrates. Subtraction of the weights of nitrates (*E*) and carbonates from *C* gives that of the extractive matters and of ammonium nitrate, if this is present; the latter may be determined in the aqueous liquid, *A*, by estimating the ammonia evolved in the ordinary way.

surrounded by a screen, *D*. The central aperture carries a thermometer, and one of the others a thermo-regulator (if necessary), whilst in the remaining ones are placed test-tubes which contain the nitrocellulose (1 to 3 grams) or nitroglycerine (2 c.c.) and dip into the water. Each of the stoppers of the test-tubes is fitted with a hook of glass tubing on which is hung a piece of starch-potassium-iodide paper moistened at the upper part with a drop of dilute glycerine.

The temperature of the bath is maintained at 82°; in France Powder *B* is tested at 110° and in other countries smokeless powders are tested up to 130°, a current of air being passed over the heated explosive. The test is finished when a faint brown coloration appears at the edge of the glycerine. A good guncotton will withstand heating at 82° for half an hour without browning the paper.

If nitrocellulose is stabilised by the incorporation with it of a little sodium bicarbonate or calcium carbonate, it becomes less stable to the Abel test.[1]

Measurement of the Pressure and Heat of the Gases Developed by Explosives. The power of an explosive is deduced principally from the quantity of heat produced on explosion (*see* p. 259), this being measured in the Berthelot-Mahler calorimetric bomb (*see* Vol. I., p. 461). Deflagration is induced by means of an electric spark, and if considerable pressure is maintained in the bomb by means of air (or nitrogen in the case of guncotton, as this is deficient in oxygen, which should not be supplied if the conditions of an ordinary explosion are to be reproduced), the products of deflagration are almost identical with those of explosion. The bomb is specially constructed with various accessories to allow of the analysis and measurement of the gases produced in the decomposition, at either low or high pressure, of the explosive.

The *pressure* of the gases produced by the explosion in a resistant chamber, *C* (Fig. 227), of soft sheet steel wrapped round with steel wire, is measured indirectly by determining the crushing of a small copper cylinder, *Z* (*crusher*), 13 mm. high and 8 mm. in diameter, placed between a fixed base, *d*, and a hardened steel piston, *a*, of known surface which transmits the pressure of the gases. The chamber, *C*, is fixed by two massive wrought-iron plates, *D* and *D′*, held together by six thick rods, *B*.

Deflagration is caused by rendering incandescent a platinum wire between the two terminals, *b*. In order to obtain exact results it is indispensable that there be no escape of the gas, which would also cause danger from projection, the gas being at a temperature of 2000° to 3000° and a pressure of several thousand atmospheres.

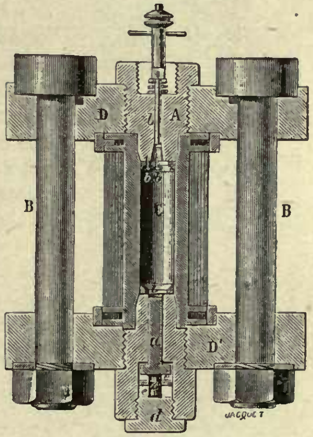

FIG. 227.

The deformation of the *crushers* is shown in almost the natural dimensions in Fig. 182 on p. 262.

The *sensitiveness* of explosives to a *blow* is determined empirically by allowing a given

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[1] According to Will (1902) and Egerton (1913), this test is very sensitive, being able to detect 0·0000016 gram of nitrous acid in 100 grams of explosive. However, some years ago certain English manufacturers added various substances (*e. g.*, mercuric chloride, formaldehyde, etc.) to mask the instability of their powders. It must also be borne in mind that the sensitiveness of the reaction may be influenced by the method of preparation of the starch-iodide powder. The test is carried out in a pure atmosphere removed from the smallest traces of nitrous acid vapour. Since decomposition in powders is gradual, the duration of the test (*e. g.*, thirty minutes) should be noted.

Angeli test: When explosives with a basis of nitric esters contain solvent (ether, alcohol, acetone, etc.) or stabilising substance, the Abel test is insufficient, since the reaction of the nitrous vapours is prevented or retarded. In 1917 Angeli proposed to replace the Abel test by a qualitative test of the acidity carried out as follows: A portion of the powder cut into thin flakes is shaken in a test-tube with water containing a few drops of a 0·2 per cent. alcoholic solution of *dimethylaminoazobenzene*, *q.v.*, Part III); if the flakes remain yellowish, they are not acid and have kept well, but if they turn red, they are acid and have undergone alteration.

Silvered vessel test: This is used in England and Italy, and consists in determining the number of hours required for the temperature of the explosive kept in a silvered flask (100 c.c. or up to 3000 c.c.) in a thermostat at 80° to rise by 2°.

weight of iron (*ram, see* Fig. 228) to fall from various heights on to a certain amount of explosive placed on an iron block, the height of the fall being increased until explosion occurs. The sensitiveness to *heat* is measured roughly by throwing small pieces of the explosive on to mercury heated to successively increasing temperatures until deflagration takes place.

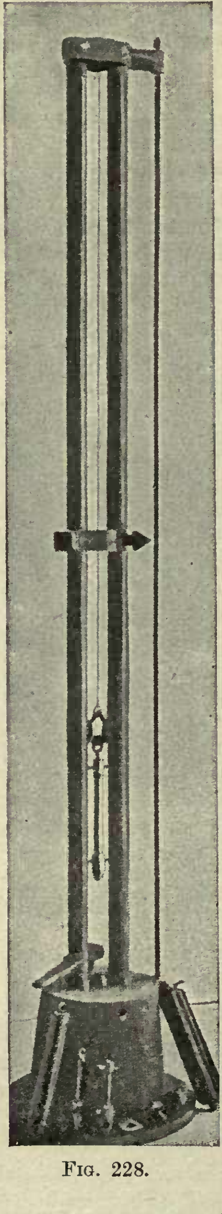

FIG. 228.

FIG. 229.

When the *power of an explosive* cannot be determined directly or by comparison of the practical effects, indirect tests must be employed, although these do not always correspond with the actual effects. To avoid uncertainty, the expression *power of an explosive, f*, is applied to the product of the volume, v_o, of gas (reduced to 0° and formed from unit weight of the explosive), the pressure, p_o, in mm., and the absolute temperature, T (calculated from the products of the reaction), this product being divided by 273, so that:

$$f=\frac{v_o p_o T}{273}.$$

The power of progressive explosives may be determined indirectly by Guttmann's power gauge (Fig. 229): on a hollow block of steel, *a* (diameter of cavity 35 mm.), are screwed two steel blocks, *b*, and a small firing-plug, *g*. A trigger, *m*, which can be released from a distance by means of a cord, serves to explode the plug. The apparatus is charged by unscrewing one of the blocks, *b*, and introducing first a cylinder of drawn lead, 40 mm. long and 35 mm. in diameter, which closes hermetically the wide mouth of the right-hand cone: then a steel disc and one of cardboard of such thickness that it makes 20 grams of powder rest just in the middle. This powder, which is introduced next, is situate just under the cap, *h*. Then follow a disc of cardboard, one of steel, and a block of lead similar to the first, this closing the cavity to the left, when the block, *b*, is again screwed on. The gases produced by the explosion have no outlet, and so force the leaden blocks into the conical holes to the right and left. The height of the leaden *cones* projecting is compared with that obtained with a standard explosive and thus gives the power of the explosive.

For shattering explosives, on the other hand, good results are obtained with Trauzl's *lead block*, which is in the form of a cylinder 200 mm. in height and diameter. In the middle is a cavity, 110 mm. deep and 20 mm. wide, into which 15 to 20 grams of the explosive is placed. A fulminate cap, connected with wires for firing, is inserted and the bore tamped with well-compressed sand and chalk. After the explosion, the capacity of the cavity is measured with water. Fig. 230 shows several of these blocks after testing with various explosives. A charge of 15 grams of No. 1 dynamite gives a volume of 705 c.c., and deducting from this 30 c.c. for the original volume, and 30 c.c. produced by the 1·5 grams of fulminate in the cap, there remains 645 c.c. due to the explosive, *i. e.*, 43 c.c. per gram. To obtain comparable results with explosives of the same class, charges of equal weights must be taken, otherwise different values are obtained for the same explosive; there are, besides, other causes of error, which give only a relative value to this method of determining the power.

FIG. 230.

Measurement of the Initial Velocity of Projectiles. For this purpose use is made of Le Boulengé's *chronograph* (Figs. 231 and 232), which gives the velocity, V, by measuring the time, T, taken by the projectile to traverse the known distance, D (20 to 50 metres), between two wire frames, G, G' (Fig. 231), which are cut through by the projectile immediately after it leaves the gun and are connected electrically with two quite distinct points of the chronograph, the apparatus being so arranged that T lies between 0·05 and 0·15 second; $V = \frac{D}{T}$. The chronograph is formed of two electro-magnets, a and e (Fig. 232, or C and C', Fig. 231), joined to the batteries B and B', and to the corresponding wire frames, G and G'. The magnet, a, attracts a tubular bar (c, d, Fig. 232, or C, Fig. 231) of the *chronometer*, which terminates at the top in a soft iron point and is enlarged at the bottom; the magnet, e (or A' in Fig. 231), attracts a rod, f (or C', Fig. 231), of the *registrar*. The chronometer bar is surrounded by a thin zinc or copper tube. The registrar is of soft iron, has the same weight as the chronometer, and is pointed at the top and enlarged at the bottom. When the projectile traverses the first frame, G, it interrupts the current of the electro-magnet, A, and the chronometer bar, C, becomes detached from A (Fig. 231) and begins to fall freely. When it traverses the second frame, G', it interrupts the current

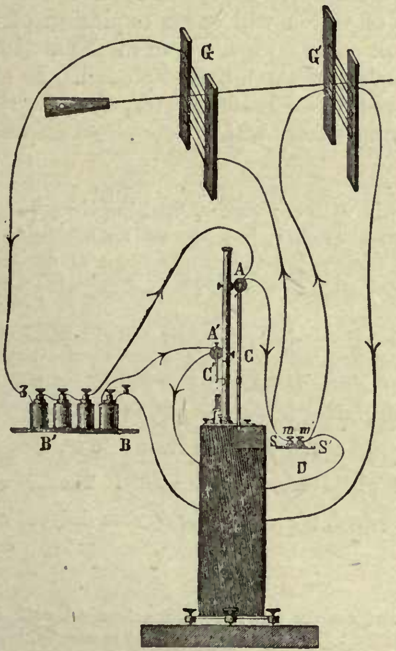

FIG. 231.

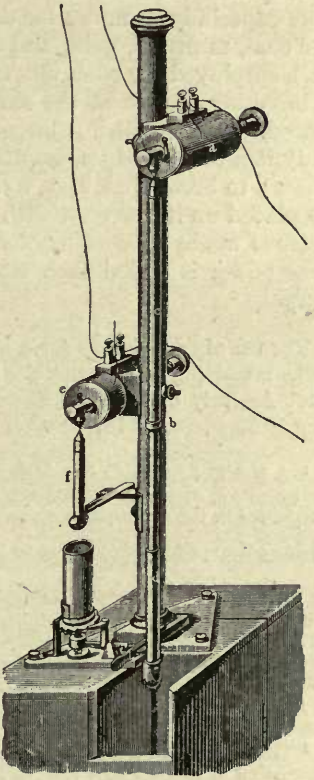

FIG. 232.

of the electro-magnet, A', and the registrar, C', falls and releases a hook which liberates a horizontal spring pointer, this immediately striking the falling chronometer bar. The mark on this bar will be the higher the lower the initial velocity of the projectile. Suitable tables deduced from simple formulæ [1] give the required velocity.

The velocity of detonation is difficult to determine, since it depends largely on the resistance of the enclosure containing the explosive and on other circumstances. It is determined roughly but with sufficient exactitude, under similar conditions, by placing a number of cartridges in a continuous row and joining the two wires of the Le Boulengé chronograph to points in the row at a certain distance apart.

USES OF EXPLOSIVES. The largest consumption of explosives is that of armies and navies, whilst in various civil operations these substances are also employed: in the tunnelling of mountain ranges; in lessening manual labour in the ploughing of the soil; for disintegrating rocks to provide material for the construction of houses to displace the all too numerous deserts; and further, for preparing blocks of material to be wrought by the genius of man into monuments attesting to posterity the varied and incessant progress of human thought and labour.

In practice a sharp distinction is made between progressive explosives, used more especially in mines for detaching large masses of rock and for excavating (for coal, minerals, gold, and diamonds), and shattering explosives (dynamite, etc.), employed for such purposes as demolishing walls, bridges, and large trees, or breaking the ice at the surface of rivers and lakes when navigation is prevented. To demolish a large tree it is sufficient to surround it with a string of dynamite cartridges, explosion of one of which will cause explosion of the others; to break iron, *e. g.*, a railway rail, or cut a bridge, one or more cartridges are placed on it, covered with a light tamping of earth and exploded. In subaqueous works modern smokeless explosives are of great service, since to their great power is added their stability towards water, which acts as an excellent tamping.[2]

The use of *explosives in agriculture*, particularly with the view of utilising the enormous stocks remaining in all countries after the European War, has become an accomplished fact. As early as 1870 De Hamm of Vienna anticipated the employment of dynamite in agriculture, and in 1878, Sobrero, in a communication to the Turin Academy of Sciences,

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[1] A test is first made in which the chronometer bar and the registrar fall simultaneously. The height, h, at which the former is struck corresponds with a time, t, which must always be allowed for in the subsequent measurements, as it represents the time required by the registrar to release the spring. According to the law of bodies falling freely, $h = \frac{1}{2}gt^2$, so that $t = \sqrt{\frac{2h}{g}}$; in practice, when a time, T, elapses during the passage of the projectile from G to G', the mark on the chronometer bar at the height, H, corresponds with a time, $T + t = \sqrt{\frac{2H}{g}}$. The difference between these two measurements gives the time required, the velocity being then deduced from the formula: $V = \frac{D}{\sqrt{\frac{2}{g}}(\sqrt{H} - \sqrt{h})}$.

[2] The Mont Cenis tunnel, which connects Italy and France, and is 12,233 metres in length, was commenced in August 1857 and, as it was assumed that the blasting would be carried out with black powder, it was calculated that twenty-four years would be required to complete the work. After 1865, however, dynamite became available, and the work was finished eleven years earlier than was anticipated, 1000 tons of explosive being used and £2,800,000 expended. The St. Gothard tunnel (14,920 metres), joining Italy and Switzerland, was completed in six years and a half (1873–1880), and cost £10,400,000.

During the piercing of the Simplon, 1640 tons of gelatine explosives were used, mostly with a content of about 92 per cent. of nitroglycerine. In constructing the harbour of Genoa, the Nobel Company exploded simultaneously a number of mines with a total charge of 6000 kilos of dynamite. For the removal in 1905 of a rock that partially obstructed the Danube at Greisenstein, a mine was laid with 11,700 kilos of dynamite; 280,000 cu. metres of rock were detached at a cost of about three-halfpence per cubic metre. In the American Independence Day fêtes, a million pounds worth of fireworks are consumed every year.

made definite proposals in this direction. Various practical applications were afterwards made in America, Germany and elsewhere, and in 1918–1919 rigorous and systematic tests, carried out by specialists in America, France and Italy (with trinitrotoluene and picric acid) showed that highly compact and semi-rocky soils may be broken down satisfactorily in this way; cartridges of 100 or 200 grams were placed less than 1½ metres apart at a depth of about 60 cm., good tamping being provided. Explosives are used economically only when the usual means present great difficulties.

In the United States a single factory produced in 1911 explosives to the value of £120,000 for agricultural purposes.

STATISTICS OF EXPLOSIVES. The consumption of explosives in time of war is enormous. Every shot of a large gun, which does not always hit the mark, costs hundreds of pounds.

The *world's production* of explosives prior to the European War reached a total of 350,000 to 400,000 tons, almost the half of this amount being made in the United States. According to O. Guttmann, the production of explosives with nitroglycerine as base amounted in 1909 to more than 62,000 tons, distributed as follows: United States, 20,000 tons (in 1912, over 22,000 tons); Germany, 10,300; England, 8100; the Transvaal, 8000; Canada, 5000; Spain and Portugal, 3500; Austria-Hungary, 2300; France, 1500; Switzerland, Australia, and Norway and Sweden, 600 each; Russia, Italy, and Holland and Belgium, about 500 each; and Greece, 175 tons.[1]

EE. ACIDS

I. SATURATED MONOBASIC FATTY ACIDS, $C_nH_{2n}O_2$

These are termed *fatty* acids because some of them are contained in fats, from which they are prepared. All contain the characteristic group, $-CO_2H$, the

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[1] The output of *military explosives* in different countries in 1913 and during the first two years of the European War is shown approximately by the following figures (tons):

	Great Britain	Germany	France	Italy	United States	Russia	Japan	Austria	Whole world
1913 .	18,000	60,000	15,000	3,500	8,000	6,000	4,000	5,000	150,000
1915 .	120,000	360,000	160,000	15,000	130,000	60,000	50,000	90,000	1,065,000
1916 .	200,000	540,000	300,000	45,000	190,000	100,000	90,000	150,000	1,805,000

In addition to its enormous home consumption, Germany exported, in 1906, 2136 tons of black powder, of the value £320,000; 4791 tons of other explosives, worth £372,000; and 7300 tons of cartridge charges for guns and artillery, of the value £1,000,000. In 1913 the total German exports of explosives were valued at £4,000,000 and the imports at £72,000. The output of dynamite in Germany was 2000 tons in 1880, 4000 in 1890, 8000 in 1909, and 11,000, besides 15,000 of safety explosives with a basis of ammonium nitrate, in 1912. Before the war, some of the German explosives factories paid dividends of 25 per cent. or more.

In the United States the industry is a rapidly growing one. While the total production was £3,400,000 (including 40,000 tons of dynamite) in 1900, it rose in 1905 to £5,920,000, of which £1,760,000 represented black powder; £320,000 nitroglycerine; £2,600,000 dynamite; £800,000 smokeless powder; and £35,200 guncotton.

In 1909 the capital invested in explosives works in the United States amounted to £10,000,000, the output comprising 85,000 tons of dynamite, 4500 tons of safety mine explosives, 14,000 tons of nitroglycerine, 6000 tons of black powder, 45,000 tons of shattering explosives, etc., the total value being £8,000,000 (in 1904, £6,000,000), and the power used 28,600 horse-power.

During the period of their neutrality, the United States manufactured enormous quantities of explosives for home consumption and for the Allies, especially France, Great Britain, and Russia. About 205,000 tons were made for home consumption in 1915, and more than 225,000 tons in 1916; the value of the exports was £2,000,000 in 1914 and £153,400,000 in 1916. When the European Allies became able to supply their own needs, the American factories continued to produce on an even vaster scale for the needs of their own country in the war.

In 1910 Great Britain exported 630 tons (£172,000) of smokeless powders and 7200 tons (£720,000) of dynamite, 450 tons (£37,600) of the latter being imported. In 1907, Great Britain consumed 7000 tons of black powder and exported 3597 tons (3500 in 1910). Before the European War single factories in England made as much as 10,000 tons of dynamite per annum.

Japan, which before the war possessed two Government factories for military explosives, imported from Great Britain and Germany various explosives, to the value of £100,000, in 1910.

In Belgium the consumption of mining explosives in 1910 was about 1473 tons, 229 tons being black powder.

In the same year Austrian mines used about 2395 tons of different explosives, 1600 tons being dynamites of various types, while in the Transvaal mines explosives to the value of £1,440,000 were consumed.

hydrogen of which is replaceable by metals. With every hydrocarbon or every primary alcohol of the methane series corresponds a monobasic fatty acid. The first members are liquids having a pungent odour, and are soluble in water, alcohol, or ether, and boil without decomposing; then follow members of an oily consistency, less soluble in water, and with unpleasant smells like that of rancid butter or perspiration; beyond C_{10} they are solid, insoluble in water, and soluble in alcohol or ether, and distil unchanged only in a vacuum. The first members (up to C_9 or C_{10}) are volatile in steam.

It will be seen from the Table that the boiling-points of these acids rise regularly with increase in the number of carbon atoms, but the melting-points are higher in an acid with an even number of carbon atoms than in those immediately below and above with uneven numbers.

TABLE OF THE SATURATED MONOBASIC FATTY ACIDS

Formula	Name	Melting-point	Boiling-point		Specific gravity	
CH_2O_2	Formic	+ 8·3°	101°		1·2187 (20°)	
$C_2H_4O_2$	Acetic	+ 16·5°	118°		1·0502 (20°)	
$C_3H_6O_2$	Propionic	− 22°	141°		1·013 (0°)	
$C_4H_8O_2$	Normal butyric	− 7·9°	162°		0·978 (0°)	
	Isobutyric	− 79°	154°		0·965 (0°)	
$C_5H_{10}O_2$	Normal valeric	− 58·5°	185°		0·956 (0°)	
	Isovaleric	− 51°	174°		0·947 (0°)	
	Trimethylacetic	+ 34°–35°	163°		0·905 (50°)	
	Methylethylacetic	—	173°–174°		0·938 (20°)	
$C_6H_{12}O_2$	Normal caproic (hexoic)	− 1·5°	205°		0·945 (0°)	
$C_7H_{14}O_2$	Normal heptoic	− 10°	223°		0·921 (15°)	
$C_8H_{16}O_2$	Caprylic (octoic)	+ 16·5°	237·5°		0·910 (20°)	
$C_9H_{18}O_2$	Pelargonic (nonoic)	+ 12·5°	186°	At 100 mm. pressure.	0·911 (12°)	
$C_{10}H_{20}O_2$	Capric (decoic)	+ 31·4°	200°		0·930 (37°)	
$C_{11}H_{22}O_2$	Undecoic	28°	212°		—	
$C_{12}H_{24}O_2$	Lauric	44°	225°		0·875	At melting-point.
$C_{13}H_{26}O_2$	Tridecoic	40·5°	236°		—	
$C_{14}H_{28}O_2$	Myristic	54°	248°		0·862	
$C_{15}H_{30}O_2$	Pentadecoic	51°	257°		—	
$C_{16}H_{32}O_2$	Palmitic	62·6°	268°		0·853	
$C_{17}H_{34}O_2$	Margaric	60°	277°		—	
$C_{18}H_{36}O_2$	Stearic	69·3°	287°		0·845	
$C_{19}H_{38}O_2$	Nonadecoic	66·5°	298°		—	
$C_{20}H_{40}O_2$	Arachidic	77°	—		—	
$C_{22}H_{44}O_2$	Behenic	84°	360°/60 mm.		—	
$C_{24}H_{48}O_2$	Lignoceric	80°–81°	—		—	
$C_{26}H_{52}O_2$	Cerotic	78·5°	—		—	
$C_{30}H_{60}O_2$	Melissic	91°	—		—	

GENERAL METHODS OF PREPARATION. (*a*) In dealing with primary alcohols and aldehydes, it was shown how simple oxidation of these compounds yields the corresponding acids containing the same number of carbon atoms, whilst when secondary and tertiary alcohols or ketones are oxidised, the chain is broken and acids with a less number of carbon atoms are obtained.

(*b*) Hydrolysis of the *nitriles* (*see these*) in the hot with potassium hydroxide or with mineral acids yields the amides (*see these*) as intermediate compounds, and then the acids with one carbon atom more than the alcohols from which the nitriles originate :

$$CH_3 \cdot CN + 2H_2O = NH_3 + CH_3 \cdot CO_2H.$$

(*c*) The interaction of a zinc-alkyl with phosgene gives:

$$Zn(CH_3)_2 + 2COCl_2 = ZnCl_2 + 2CH_3\cdot COCl \text{ (Acetyl chloride)},$$

which on decomposition with water gives:

$$CH_3\cdot COCl + H_2O = HCl + CH_3\cdot CO_2H.$$

(*d*) When a hydroxy-acid is heated with hydrogen iodide, separation of water and iodine occurs and a fatty acid is formed.

(*e*) Other general reactions are those of Grignard (*see* pp. 33, 243), those of ethyl acetoacetate and ethyl malonate (*see these*), and those of elimination of CO_2 from dibasic acids (containing two carboxyls, CO·OH) and of addition of hydrogen to unsaturated acids, etc.

PROPERTIES. In aqueous solution the acids are electrolytically dissociated into the *cations* H and the *anions* $R\cdot CO_2$ (*see* Vol. I., p. 94).

Substitution of this ionic hydrogen by a metal yields *salts*, which in aqueous solution (when they are soluble) are almost completely dissociated, whilst the hydrogen of the hydroxyl group of the alcohols is also replaceable by a metal (alkoxide), but the resulting alkoxide is decomposed by water (hydrolysed).

The strength of an acid (or its power) may always be determined from the degree of dissociation (Vol. I., pp. 95, 102), this decreasing in the following order: formic, acetic, propionic, normal butyric, valeric, etc.; thus, with rise of the molecular weight the dissociation diminishes.

The hydroxyl group of the carboxyl group, —CO · OH, may sometimes be substituted by halogens (especially by chlorine, by the action of PCl_5, which forms acid chlorides or *chloroanhydrides*, *e. g.*, acetyl chloride, $CH_3\cdot COCl$).

Substitution of the hydroxyl, (1) by SH, gives *thio-acids*, and (2) by NH_2 yields the *amides*, *e. g.*, acetamide, $CH_3\cdot CO\cdot NH_2$ (by heating ammonium acetate); under certain conditions these compounds all give the acids from which they originate.

It has already been mentioned that the saturated hydrocarbons are formed by the electrolysis of the alkali salts of the corresponding acids, with elimination of CO_2, H, and O (the last two from the water present as solvent) and also of secondary products (unsaturated ethers and hydrocarbons); if the electrolysis is effected without a diaphragm, alkali carbonate and bicarbonate are formed, and hence also a lower alcohol. Carbon dioxide may also be eliminated, and hydrocarbons thus formed, from the alkali salts of the acids by heating in presence of soda-lime or baryta, or by reducing the acids with hydriodic acid and phosphorus.

If, however, the calcium salts of the acids are distilled, with or without P_2O_5, the principal product is a ketone formed from two molecules of the acid:

$$(CH_3\cdot COO)_2Ca = CaCO_3 + CH_3\cdot CO\cdot CH_3;$$

if the calcium salt is heated in presence of calcium formate, the aldehyde corresponding with the higher acid is formed.

The halogens also replace the hydrogen of the alkyl residues of the acids, giving products which surpass in acid properties the acids from which they are formed.[1] By heating the acids homologous to acetic acid (which are very

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[1] Besides referring to what has been stated in Vol. I., pp. 98 *et seq.*, we may here quote the very clear consideration of this question given by Miolati in a publication on the Affinity Constants of Acids. That different acids possess different strengths follows, for example, from the phenomenon of displacement of one acid from its salts by another acid. When sulphuric acid is added to a solution of sodium acetate, the characteristic odour of acetic acid is perceived, since the sulphuric acid is transformed into sodium sulphate and a certain amount of acetic acid is liberated. This quantity and, in general, the quantity of any acid displaced by a second acid, is not equivalent to the amount of the latter added, but the two acids divide the base according to their strengths, *i. e.*, according to their affinity constants, and also to their quantities. The effect of the latter factor may be eliminated by using equivalent quantities of the two acids and of the base, *e. g.*,

resistant to oxidising agents) with concentrated sulphuric acid, CO_2 is evolved, whilst acids with carboxyl united to a tertiary carbon atom (*e. g.*, formic or

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by causing an equivalent of an acid to act on an equivalent of neutral salt, so that the distribution of the base between the two acids depends only on their strengths. A chemical equilibrium is then established which is represented by the equation :

$$(1 - x)[NaX + HX'] \rightleftarrows x[NaX' + HX].$$

In order that this method may give exact results, it is of course necessary that the bodies formed in the conditions of the experiment be not eliminated as either gas, or solid, or complex molecules, etc., but that they remain to take part in the equilibrium. To determine this, Thomsen made use of the thermal change and Ostwald of the changes of volume and the indices of refraction, these methods leading to the same results. In general, any physical property may be used for the analysis of the equilibrated system.

If, for example, a is the heat-change observed on neutralising an equivalent of the first acid with a base, b the corresponding quantity for the second acid, and c that observed on adding an equivalent of base to an equivalent of the mixed acids, it is evident that c will be equal to the thermal effect of the neutralisation of a certain fraction of an equivalent of the first acid $(1 - x)$ plus the thermal effect of the neutralisation of the complementary fraction of the second acid :

$$c = (1 - x)a + xb; \quad x = \frac{a - c}{a - b}; \quad (1 - x) = \frac{c - b}{a - b}.$$

$\frac{x}{(1 - x)}$ is a measure of the relative affinities of the two acids. The following Table gives certain values of x determined by Ostwald, x indicating the fraction of the molecule of base taken up by the acid given first :

	x		x
$HNO_3 : CHCl_2 \cdot COOH$	0·76	$H \cdot COOH : CH_3 \cdot COOH$	0·76
$HCl : CHCl_2 \cdot COOH$	0·74	$H \cdot COOH : C_2H_5 \cdot COOH$	0·79
$CCl_3 \cdot COOH : CHCl_2 \cdot COOH$	0·71	$H \cdot COOH : C_3H_7 \cdot COOH$ norm.	0·80
$CCl_3 \cdot COOH : CH_2Cl \cdot COOH$	0·92	$H \cdot COOH : C_3H_7 \cdot COOH$ iso.	0·81
$CCl_3 \cdot COOH : H \cdot COOH$	0·97	$CH_3 \cdot COOH : C_3H_7 \cdot COOH$ (norm.)	0·53

If we calculate $\frac{x}{1 - x}$, making nitric acid equal to 100, we obtain the following values :

Nitric acid	100	Formic acid	3·9
Hydrochloric acid	98	Propionic acid	1·04
Trichloroacetic acid	80	Butyric acid	0·98
Dichloroacetic acid	33	Glycollic acid	5·0
Monochloroacetic acid	7	Lactic acid	3·3
Acetic acid	1·23		

The acids arrange themselves in the same order and almost with the same coefficients, if other properties are studied. All acids possess, for example, the property of accelerating certain hydrolyses, such as that of ethyl acetate and the inversion of cane-sugar :

$$CH_3 \cdot COOC_2H_5 + H_2O = C_2H_5 \cdot OH + CH_3 \cdot COOH;$$
$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

In these reactions the acid added acts only by its presence (catalysis), since at the end of the reaction it remains unchanged. On addition of equivalent quantities of various acids, however, the reactions take place with greater or less velocities, *i. e.*, the same quantity of ethyl acetate or cane-sugar is transformed in a longer or shorter time according to the acid added. The velocity of the reaction is proportional to the affinity constant of the acid. Finally, the acids are arranged in the same order if we compare their electrical conductivities. According to the theory of electrolytic dissociation, the value of the conductivity depends on the number of molecules of the dissolved acid which are dissociated into their ions, *i. e.*, into hydrogen ions on the one hand, and acid ions on the other. *The possibility of furnishing hydrogen ions in aqueous solution would hence be characteristic of the acid nature of a substance, the amount of these hydrogen ions in unit volume being a measure of the acidity.* With equivalent solutions of different acids, the strong acids will be those which contain, in a given volume of the solution, a large number of hydrogen ions, and the weak ones those containing only a small number of such ions.

The condition of an acid in solution may hence be represented by the expression :

$$AH \rightleftarrows A' + H^{\cdot}$$

and we may term the fraction of the equivalent which is dissociated, the *degree of dissociation*, α. Without entering into further details it may be mentioned that α is related, besides to the electrical conductivity, also to van 't Hoff's coefficient i, which expresses the divergence of the osmotic behaviour of solutions of electrolytes from the normal behaviour (*see* Vol. I., p. 102).

The degree of dissociation varies with the concentration of the solution of the acid, increasing with the dilution towards the limiting value 1, which corresponds with complete dissociation.

trimethylacetic acid) evolve CO and are transformed by oxidising agents into hydroxy-acids : $(CH_3)_2 : CH \cdot COOH$ gives $(CH_3)_2 : C(OH) \cdot COOH$.

This increase is small for strong acids, *i. e.*, those which contain a considerable number of hydrogen ions even in concentrated solutions, but is much greater for the weak acids.

	v	100 α	
$CH_3 \cdot COOH$	32	2·38	1
	1024	12·66	4·22
$CH_2Cl \cdot COOH$	32	19·9	1
	1024	68·7	3·53
$CHCl_2 \cdot COOH$	32	70·2	1
	1024	99·7	1·42

v indicates the number of litres of solution containing 1 gram-mol. of the acid.

The affinity constants given above hence depend on the concentration of the acid, since with this the concentration of the hydrogen ions—on which the value of the acid properties of a substance depends—varies. An expression which is independent of v may, however, be found by considering the equilibrium : $HA \rightleftarrows H^{\cdot} + A'$, as if it were a gaseous equilibrium and applying the law of mass action to it. If α is the fraction of the equivalent which is dissociated, $(1 - \alpha)$ will be that of the non-dissociated part; and, if v is the number of litres in which the gram-equivalent is dissolved, $\frac{\alpha}{v}$ will be the so-called active mass of the ions, *i. e.*, the number of ions contained in unit volume, and $\frac{1-\alpha}{v}$ the number of undissociated molecules in the same unit volume. The law of mass action gives :

$$\left(\frac{1-\alpha}{v}\right)k = \left(\frac{\alpha}{v}\right)\left(\frac{\alpha}{v}\right); \quad k = \frac{\alpha^2}{(1-\alpha)v},$$

where k is a constant depending solely on the nature of the equilibrium—that is, on the nature of the reacting bodies—and on the temperature; k is hence a measure of the tendency of an acid to dissociate and is called the *affinity constant.*

The following Table gives the numbers referring to acetic acid and two of its chloro-derivatives :

v	Acetic Acid			Monochloroacetic acid			Dichloroacetic acid		
	Δ	100 α	$10^5\,k$	Δ	100 α	$10^5\,k$	Δ	100 α	$10^5\,k$
16	6·5	1·67	1·79	56·6	14·6	155	—	—	—
32	9·2	2·38	1·82	77·2	19·9	155	269·8	70·2	5170
64	12·9	3·33	1·79	103·2	26·7	152	309·9	80·5	5200
128	18·1	4·68	1·79	136·1	35·2	150	338·4	88·0	5040
256	25·4	6·56	1·80	174·8	45·2	146	359·2	93·4	5160
512	34·3	9·14	1·80	219·4	56·8	146	375·4	97·6	—
1024	49·0	12·66	1·77	265·7	68·7	147	383·8	99·7	—

In this Table Δ denotes the molecular conductivity corresponding with the dilution v, 100 α the extent of dissociation in per cent., and $10^5\,k$ the affinity constant multiplied by 100,000.

This affinity constant has a markedly constitutive character; it increases, for instance, if a substituent of negative nature, such as OH, Cl, N, NO_2, etc., enters a molecule and decreases if positive groups such as NH_2 enter. The following examples may be given :

Formic acid	$k = 127{\cdot}0 \,.\, 10^{-5}$
Acetic acid	$1{\cdot}8 \,.\, 10^{-5}$
Propionic acid	$1{\cdot}3 \,.\, 10^{-5}$
Substitution with halogens and similar groups.	
Monochloroacetic acid	$k = 155 \,.\, 10^{-5}$
Dichloroacetic ,,	$= 5100 \,.\, 10^{-5}$
Trichloroacetic ,,	about $120{,}000 \,.\, 10^{-5}$
Bromoacetic ,,	$138 \,.\, 10^{-5}$
Cyanoacetic ,,	$370 \,.\, 10^{-5}$
Thiocyanoacetic ,,	$260 \,.\, 10^{-5}$
β-Iodopropionic ,,	$9{\cdot}0 \,.\, 10^{-5}$
Substitution by hydroxyl.	
Glycollic acid, $OH \cdot CH_2 \cdot COOH$	$k = 15{\cdot}0 \,.\, 10^{-5}$
Lactic acid, $CH_3 \cdot CH(OH) \cdot COOH$	$14{\cdot}0 \,.\, 10^{-5}$
β-Hydroxypropionic acid, $OH \cdot CH_2 \cdot CH_2 \cdot COOH$	$3{\cdot}1 \,.\, 10^{-5}$
Substitution by NH_2.	
α-Aminopropionic acid (alanine), $CH_3 \cdot CH(NH_2) \cdot COOH$	$k = 9{\cdot}0 \,.\, 10^{-5}$

For further examples and greater details, *see* R. Abegg's "The Electrolytic Dissociation Theory." New York, 1907.

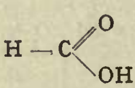
Separation of the fatty acids from mixtures of them is not always easy, and is sometimes effected by taking advantage of their greater or less volatility either in steam or in a vacuum, or by precipitating with magnesium acetate or barium chloride, since in alcoholic solution the higher acids are precipitated first. Use is also made of the fractional solution of the calcium, barium, or lead salts in various solvents (alcohol, ether, etc.), or of fractional neutralisation followed by distillation of the acids not neutralised. From an aqueous mixture of formic, acetic, butyric, and valeric acids, the last two may be separated by extraction with benzene, from which they may be isolated by shaking with baryta water. Further separation may then be effected as above.

Constitution of the Fatty Acids. That these acids actually contain carboxyl groups, —COOH, is indicated by the different ways in which they are formed and decomposed, but the most characteristic method of preparation consists of the hydrolysis of the nitriles, which are obtained from the alkyl iodides by the action of potassium cyanide (*see* p. 238). Two molecules of water react with one of nitrile, giving ammonia and a higher acid :

$$CH_3 \cdot C \vdots N + 2H_2O = NH_3 + CH_3 \cdot COOH.$$

The nitrogen of the nitrile being detached, the group —COOH must necessarily be formed, since, from reasons already mentioned, the formation of a group $-C(OH)_3$ is excluded, as three free hydroxyl groups cannot remain united to one carbon atom (although the corresponding *ortho-ethers* are known and also acetals, *see* pp. 217, 251 and 252).

FORMIC ACID,



$H-C\langle^{O}_{OH}$

Methanoic Acid

It was shown as early as the seventeenth century that ants contained a special acid, which was characterised later as formic acid, and was separated (by distilling with water) from the wood ant, the migratory ant, bees (and hence from crude honey), the hairs of the nettle, pine leaves, perspiration, urine, etc.

Gerhardt was the first, in 1850, to show that CO_2 and formic acid are obtained when oxalic acid is heated in presence of sand. In 1855 Berthelot, and later Lorin obtained good yields of the acid in 60 per cent. or even 75 per cent. concentration by heating crystallised oxalic acid with anhydrous glycerol in a reflux apparatus; this reaction yields first CO_2, H_2O and formic acid in the form of glyceride, $HCO_2[C_3H_5(OH)_2]$, this being hydrolysed by the water of crystallisation of a further quantity of the oxalic acid, with regeneration of the glycerol and liberation of formic acid. For 100 kilos (220 lbs) of formic acid, 300 kilos (660 lbs) of oxalic acid are consumed. For some years formic acid has been more economically obtained by decomposing formates prepared synthetically.

In 1856, Berthelot found that a minimal amount of formic acid is obtained when CO acts on concentrated sodium hydroxide solution at 200°. Better yields were procured in 1880 by Merz and Tibiriçà by the use of powdered caustic soda (as soda-lime with 6 per cent. of moisture) at 200°. 392°F

The CO may be used in the form of producer gas. In 1894 Goldschmidt (Ger. Pat. 86,419) obtained a better yield, even at 50° (120°F) to 70° (160°F), by allowing the CO to act under a pressure of 6 to 7 atmos. on powdered caustic soda, which does not melt at such temperatures.[1]

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[1] Even before purification, producer gas (*see* Vol. I., p. 489), should contain about 30 per cent. of CO, less than 1 per cent. of CO_2, 69 per cent. of N, and traces of sulphur compounds. Since plants to yield 3000 kilos of sodium formate per day are commonly employed, the theoretical requirements amount to 1330 kilos of CO, or about 4000 cu. metres of producer gas, obtained from about 800 kilos of coke; in practice use is made of producers giving 350 cu. metres (*i. e.*, 500 kilos, consisting of 130 kilos of CO and 370 kilos of N) of gas per hour (70 kilos of coke), so as to allow for a practical consumption double of the theoretical. Owing to the loss of CO, which is poisonous, during the purification and manufacturing operations, efficient ventilation is necessary, and cylinders of oxygen are kept for artificial respiration in cases of poisoning. The producer has to be in action for three to four hours before it gives a gas of the desired composition,

The reaction is carried out in horizontal, cylindrical, double-walled autoclaves, which hold about 2000 litres, are about 2 metres long and 1·3 metres in diameter, and are constructed of 15 to 18 mm. sheet-iron, capable of withstanding internal pressures of 10 atmos. A charge of 2000 kilos of caustic soda yields about 3000 kilos of sodium formate, three autoclaves, and a fourth one as a spare, being required for this amount. The heating lasts thirty hours, and six hours are allowed for charging and discharging. The autoclaves are furnished with stirrers to prevent the formation of lumps, the gas being passed in slowly. For a couple of hours the temperature is kept at 120° to 130°, but the reaction then becomes so vigorous that the steam is shut off from the jacket of the autoclave (which withstands 4 atmos.), which is then cooled to maintain the temperature constant. A suitable arrangement of valves allows of the exit of the nitrogen, almost pure at first, but rich in CO later. The mass soon becomes pasty, being composed of a mixture of sodium formate and caustic soda, and to prevent it from setting to a very hard mass it is essential that the stirrer is kept in motion to the very end of the reaction; if setting does occur it becomes necessary to dissolve the whole mass in water.

78 inches 51 inches 150 lb 4400 lbs 6600 lbs 248°F 265°F

If the producer gas contains even small proportions of sulphur compounds the mass smells of mercaptan and becomes red, the reaction remaining incomplete and the operation being spoiled. A successful operation yields a coarse, powdery, yellowish or almost white mass, which irritates the eyes and contains 90 to 94 per cent. of formate, 1 to 2 per cent. of water, 0·1 to 0·7 per cent. of NaOH, and 2 to 7 per cent. of Na_2CO_3; the final yield may amount to 95 per cent. of the theoretical. Exact analysis of the product is necessary before the formate is transformed into formic acid, and, if carried out before the mass is removed from the autoclave, serves also to show if the reaction between the NaOH and CO is finished.[1]

If the formate is not converted immediately into formic acid, it is stored in tightly-closed vessels, since otherwise it absorbs moisture and forms very hard blocks showing superficial deliquescence.

The sodium formate thus obtained is moderately pure and contains only sodium carbonate and hydroxide as impurities. The content of formate is determined by titration with permanganate in neutral or faintly alkaline solution.

Free formic acid containing 85 to 98 per cent., or even 100 per cent., of $H \cdot CO_2H$ (as marketed), is obtained by decomposing the dry sodium formate with concentrated sulphuric acid (which, however, decomposes part of the formic acid into CO_2 and H_2O, this occurring slightly in the cold, but rapidly in the hot), and distilling off the formic acid. When sulphuric acid of 60° Bé. is used no such decomposition takes place, but less concentrated formic

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and since it must be cleaned out completely every eight hours, a gasometer is necessary in order to prevent interruption of the working. The air for use in the producer should be pre-heated by means of the gas or of the outside of the producer.

The gas should be very carefully purified to remove ash, sulphur compounds and carbon dioxide (of this not more than 0·1 per cent. should remain), apparatus similar to that described on p. 50 for the purification of coal-gas being employed. After purification the gas is collected in a gasometer, from which it is drawn to the compressor to be compressed to 8 atmos. and passed on to the pressure reaction vessels. Any gas unavoidably escaping from the piping, cocks and safety valves is passed into pipes which open above the roof. Before compression, the gas is passed through wood-wool, which retains moisture and dust.

[1] According to Ger. Pat. 179,515 the manufacture is carried out as follows: The lump caustic soda, with the natural moisture of about 4 to 5 per cent., is introduced into an iron apparatus fitted with a stirrer, a current of CO being passed in, with the initial temperature 100° to 120°. The sodium formate produced on the surface of the lumps of soda is detached in powder by the movement of the mass and fresh surfaces of caustic soda thus exposed to the action of the CO. When about two-thirds of the soda is transformed into formate, the powder of the latter is collected into masses by addition of water (about 2 per cent. on the weight of the caustic soda), the residual caustic soda being thus cleaned and subsequently converted almost entirely into formate. In this way the reaction becomes so rapid and energetic that cooling, rather than heating, of the mass is rendered necessary.

300°F

On the other hand, according to Ger. Pat. 209,417, caustic soda solution of 20° Bé. at 150° to 170° is allowed to flow down a tower filled with a subdividing material, a current of producer gas being passed upwards. This process gives continuous production of formate solution (if a battery of towers in series is used), the residual nitrogen, almost devoid of CO, issuing at about 170°; as this gas is saturated with water-vapour, the water withdrawn from the solution is gradually replaced in order to maintain the concentration best adapted for the absorption of CO and for preventing the formation of incrustations. Alternatively, gas previously compressed and mixed with the required amount of steam is passed into the caustic soda. Calcium formate may be obtained by the action of milk of lime on coke at 250°.

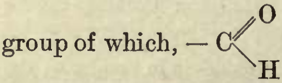
acid (60 to 65 per cent., this being inapplicable to certain condensation reactions and troublesome to transport) results; it is not possible to obtain the concentrated acid by fractional distillation of the more dilute, since when a concentration of 70 to 75 per cent. is reached, water and acid distil together in constant proportions (*see later*). To prevent decomposition by concentrated sulphuric acid Hamel (Ger. Pat. 169,730) allows sulphuric acid of 66° Bé. (75 kilos per 100 kilos of the formate) to run, slowly and with cooling, into the formate dissolved in its own weight of 90 per cent. formic acid; to the mass may be added alternately several successive quantities of 75 kilos of sulphuric acid and 100 kilos of the formate, this procedure being continued until the vessel is filled. From the stirred mixture normal sodium sulphate separates.[1] The decanted liquid mass is distilled from copper vessels and condensed in earthenware coils or receivers. In this way 90 per cent. formic acid is produced, but 100 per cent. acid may be obtained if 98 to 100 per cent. formic acid and monohydrate or slightly fuming sulphuric acid is used for the initial mixture. Almost anhydrous acid may be obtained also by distilling the 90 per cent. acid over anhydrous copper sulphate (3 : 1) (Ger. Pat. 230,171, 1909).

Hempel (Ger. Pat. 247,490) proposes to treat the crude formate immediately it is removed from the autoclave in which it is prepared (but after complete drying in a vacuum in the autoclave itself); it is discharged, after cooling, into a vessel into which a jet of finely disintegrated sulphuric acid is passed, the mass being intimately mixed. A little formic acid is previously added to the crude formate to neutralise the small amounts of free alkalies present. This process is the most economical and if properly conducted gives moderately good yields.

Formic acid from the first distillation contains minimal proportions of dissolved sulphate, HCl and S, but serves for almost all practical uses. It is obtained purer by redistilling it, and if a rectifying column is employed, 100 per cent. acid may be obtained even from 90 per cent. acid, the residue remaining then consisting of 75 per cent. acid (which distils unaltered unless mixed with dehydrating agents, such as concentrated sulphuric acid, anhydrous copper sulphate or oxalic acid, etc., the losses being then considerable).

The acid may be titrated with caustic soda solution in presence of phenolphthalein.

Pure formic acid is a colourless liquid with a pungent odour, sp. gr. 1·223 at 0° or 1·2213 at 20°; it solidifies on cooling and then melts at 8·3°, and boils at 100·6° at 760 mm. or at 30° at 50 mm. pressure. If poured on the hand it produces very painful blisters. In water it is twelve times as highly dissociated as acetic acid, and is hence a strong acid; it dissolves well also in alcohol and ether. In aqueous solution, when the concentration reaches 77·31 per cent., corresponding with the composition, $4H \cdot CO_2H + 3H_2O$, a mixture of constant composition distils, as is the case with hydrochloric acid (Vol. I., p. 166); at ordinary pressure this mixture boils at 107°. Unlike its homologues (acetic, butyric acid, etc.), it is readily oxidised by permanganate, etc., forming CO_2 and H_2O; hence its great *reducing power*, owing to which, in the hot, it separates silver from silver salts, and first mercurous chloride, and then mercury from mercuric chloride solutions. Thus it behaves as an aldehyde, the characteristic group of which,



$— C\begin{matrix} /\!\!/ O \\ \diagdown H \end{matrix}$

it does indeed contain. When heated in a sealed tube at 160° or treated with concentrated sulphuric acid, it decomposes readily and completely into $CO + H_2O$. Finely divided rhodium, ruthenium, or

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[1] Maquenne proposed the addition of 100 per cent. sulphuric acid to 85 per cent. formic acid in such quantity as to form $H_2SO_4 + H_2O$, the mass being well cooled meanwhile; this mixture is thoroughly mixed with the formate, and the formic acid then distilled. This process permits of the decomposition of unlimited quantities of formate, and not merely of that soluble in formic acid.

According to Ger. Pats. 182,776 and 193,509 the decomposition may be effected also by sodium bisulphate, 200 parts of the latter (well powdered) being mixed with 100 parts of the formate, and the formic acid distilled from a still provided with a stirrer; the residue consists of sodium sulphate. This process and the previous one have not given satisfactory results in practice.

Formates may be decomposed also by hydrofluoric acid (Ger. Pat. 209,418, 1907), or by phosphoric acid at temperatures below 145° [U.S. Pats. 970,145 of 1910 (Walker) and 975, 151].

iridium (but not platinum or palladium) decomposes it partially in the cold and completely at 200° to 300° into CO_2 and H_2; under certain conditions it yields a small proportion of *aldehyde*, but not in sufficient quantity to be of practical importance. Various bacteria produce the same change. The vapour of formic acid is inflammable and chars paper; with air it may yield detonating mixtures, so that the factories must be well ventilated and lighted by electricity.

USES OF FORMIC ACID. As formates it is largely used for making oxalic acid, while enormous amounts of free formic acid are used in 85 to 90 per cent. concentration [1] in the dyeing industry, since, owing to its low molecular weight, it competes with acetic acid, a less quantity being required to give a certain acidity.

On account of its acid character and its reducing and antiseptic properties, it is used as an antiseptic in wine-making and brewing; it is also employed to increase the yield of alcoholic fermentations, where it can replace lactic acid (not always advantageously).

Besides in the dyeing of wool, silk and woollen and cotton fabrics (as it does not attack them), it is used with advantage to replace oxalic acid, lactic acid and cream of tartar in mordanting wool, since it reduces chromic acid more slowly and more completely, exhausting the baths and thus economising dichromate (1·5 per cent. in place of 3 per cent.); in presence of formic acid wool is dyed more uniformly than with acetic acid. In the tanning industry it serves well to eliminate lime even from the most delicate hides, calcium formate dissolving well in water.

Its use in large quantities has been anticipated for making cellulose formate or *formylcellulose*, which in some cases may replace cellulose acetate (Ger. Pat. 189,837), and to prepare formic ester of glycerol (*diformin*) as a substitute for acetin (Ger. Pat. 199,873). It may be used also for making *allyl alcohol* by heating it with glycerol.

STATISTICS AND PRICES. Before the European War the price for commercial 25 per cent. formic acid (sp. gr. 1·064), was £12 per ton; for 50 per cent. (1·124), £22; for 75 per cent. (1·170), £31; for 85 per cent. (1·190), £36; and for 96 to 98 per cent. (1·217), £54. The chemically pure acid at the same concentrations cost more than double.

For large contracts the commercial 90 per cent. acid fell in price in 1913 to £22 to £24 per ton, and competed keenly with acetic acid, which was largely replaced, especially in France, in the dyeing of wool and silk.

In 1913 the German output, from six factories, was estimated at 5000 tons; in Russia there were three factories, in Switzerland two, in France two, and one each in England, the United States, Holland and Austria. Early in 1920 the Società Italiana Prodotti Esplodenti started a factory at Cengio.

Presence of hydrochloric acid as impurity may be detected by dilution (1 : 20) and addition of silver nitrate : oxalic acid may be detected by neutralising with ammonia and adding calcium chloride. If no acroleïn or allyl alcohol is present, it does not give a pungent odour after neutralisation with caustic soda.

SALTS OF FORMIC ACID are called *formates* and are generally soluble in water and crystallisable; almost all the characteristic properties and reactions of formic acid (reduction, etc.) are shown also by its salts. With concentrated sulphuric acid in the hot, they yield carbon monoxide. Formates are obtained by the action of carbon monoxide on

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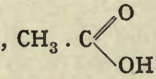
[1] Its strength is determined by means of standard sodium hydroxide solutions, using phenolphthalein as indicator, but when other acids are also present it is titrated with permanganate in alkaline solution or with chromic acid in acid solution. The CO evolved when it is treated with concentrated sulphuric acid may also be measured. When other organic acids are present, the dilute mixture is treated with mercuric acetate at the boiling temperature, the mercurous acetate which separates being filtered off in the cold and dissolved in nitric acid, the calomel precipitated with sodium chloride then being weighed. Alternatively, dilute formic acid solution (0·2 gram per litre) may be treated with about 15 times the weight of mercuric chloride (calculated on the acid) dissolved in 200 c.c. of hot water, the liquid being well shaken and the mercurous chloride precipitate, after treatment with caustic soda, collected on a Gooch crucible, washed, dried, and weighed; multiplication of the weight by 0·097726 gives the weight of formic acid (Franzen and Greve, 1909). Formic acid may be detected, even in presence of aldehydes, acetic acid, and methyl alcohol, by means of sodium bisulphite solution, which gives a reddish-yellow coloration.

metallic hydroxides in the hot and under pressure (*see* also Fr. Pat. 382,001, 1907, and U.S. Pat. 875,055, 1907). When heated at 200° to 400°, the alkali formates yield carbonates and oxalates and chemically pure hydrogen. *Potassium formate*, $H{\cdot}COOK$, forms deliquescent crystals, m.-pt. 150°. *Sodium formate*, $H \cdot COONa$, crystallises well with $3H_2O$ at 0° or with $2H_2O$ at 17°, and the anhydrous salt melts at 200° (the pure salt costs 3*s.* 7*d.* per kilo, and the commercial salt 1*s.* 7*d.*). *Ammonium formate*, $H \cdot COONH_4$, melts at 115° and at a higher temperature decomposes into formamide, water, and a little hydrocyanic acid; since, in its decomposition when heated, it gives nitrogen and carbon compounds, it is used to harden and cement steel (the pure salt costs as much as 9*s.* 6*d.* per kilo). The magnesium, barium, and calcium salts are also soluble in water; the last costs 4*s.* (pure) or 2*s.* (impure) per kilo. *Lead formate*, $(H \cdot COO)_2Pb$, dissolves only slightly in cold water, but readily in hot, and hence serves well to separate formic from other acids. *Acid formates*, such as $H \cdot COONa + H \cdot COOH$, are also known. *Silver formate* is insoluble in water.

ETHYL FORMATE, $H \cdot CO_2C_2H_5$, is a colourless, volatile, inflammable liquid, sp. gr. 0·948, b.-pt. 54·4°. It is obtained by heating in a reflux apparatus for ten hours at 80°, and stirring continually a mixture of 2 parts of alcohol, 3 parts of sodium formate, and 10 parts of powdered sodium bisulphite, the ester being finally distilled. It has the odour of arrack, and is used as artificial *essence of rum* and also in the treatment of laryngitis and acute catarrh.

The *methyl ester* boils at 32·3° and is used as a solvent for acetylcellulose.



ACETIC ACID, $CH_3 . C\begin{matrix} /\!\!/ O \\ \backslash OH \end{matrix}$

Ethanoic Acid

Although its constitution was first determined by Berzelius in 1814, acetic acid has been known from the earliest times, since it forms easily in wine (vinegar), in many vegetable juices, in sour milk, in perspiration, in excreta, etc. In 1700 Stahl obtained it in a concentrated form by freezing the dilute acetic acid, then neutralising with alkali and distilling the acetic acid after addition of sulphuric acid. It is often formed in the oxidation and combustion of many organic substances; of the various synthetic processes for its preparation, that of Kolbe (1843) may be mentioned: perchlorethane, in presence of water and under the influence of light, gives trichloroacetic acid: $CCl_3 \cdot CCl_3 + 2H_2O = 3HCl + CCl_3 \cdot COOH$, and this is reduced by nascent hydrogen to acetic acid. Commercially it is obtained from ethyl alcohol and especially by the dry distillation of wood (*see later*).

PROPERTIES. When pure, acetic acid forms a colourless liquid of sp. gr. 1·0553 at 15° and specific heat 0·522 between 26° and 96°; it solidifies at +16·7° in white crystals (hence the name *glacial acetic acid*), which are very hygroscopic and have the sp. gr. 1·08 at 0°; it boils at 118°, but evaporates considerably below this temperature owing to its high vapour pressure. It is soluble in all proportions in water, alcohol, and ether. It is one of the strongest organic acids and dissolves calcium carbonate with evolution of carbon dioxide. Its vapours burn with a bluish flame. It dissolves many organic and several inorganic substances (P, S, HCl, Fe, Al, etc.).[1] When pure concentrated acetic acid is mixed with water, heating and contraction take place; the specific gravity increases on dilution of the pure acid and reaches a maximum (1·0748) with 77 per cent. of the acid (corresponding with the hydrate, $C_2H_4O_2 + H_2O$), after-

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[1] Acetic acid readily attacks the common metals, especially iron, but if the latter is in the form of siliceous cast-iron containing about 14 per cent. of silicon and 0·9 per cent. of carbon (as in *tantiron*, *ironac*, and *helianite*), it is moderately resistant. Pure silver withstands the action of the acid well, and copper is only slightly attacked if it is kept shiny and unoxidised. Plant used in working with acetic acid is often of stoneware, which stands well if not exposed to considerable and rapid changes of temperature; quartz apparatus is able to withstand also such temperature changes (*see* Vol. I., pp. 501, 741).

wards diminishing gradually as the dilution increases.[1] Hence when the density of an acetic acid solution is given it must be indicated whether it refers to solutions containing more or less than 77 per cent. of the acid. It cannot, however, be assumed that a chemical compound, $C_2H_4O_2 + H_2O$, actually corresponds with the maximum density of the aqueous solution, since at other temperatures the maximum densities correspond with different compositions; thus, at 0° the maximum density is obtained with 80 per cent. of acetic acid and at 40° with 75 per cent. The *strength* of acetic acid generally refers to the weight and not to the volume of the acid.

The lowest freezing-point is obtained (−27°) with the aqueous solution containing 60 per cent. of the acid (corresponding with a hydrate, $C_2H_4O_2 + 2H_2O$), whilst solutions with 84 per cent. and with 10 per cent. freeze at −3·2°. Unlike those of formic acid and of mineral acids, aqueous solutions of acetic acid yield no distillate of constant composition.

The vapour density of the acid indicates a mixture of simple and double molecules below 250°, and simple molecules alone above this temperature. With hydrogen bromide it forms reddish crystalline additive products, *e. g.*, $CH_3 \cdot COOH, Br_2, 4HBr$. Certain bacteria decompose it into $CH_4 + CO_2$.

In contact with red-hot pumice, acetic acid vapour only partially decomposes, giving acetone, CO_2, and a little phenol and benzene. Chlorine replaces first one atom and then three atoms of hydrogen in the CH_3 group; bromine acts similarly at 120°, but iodine does not react. It resists in the cold the action of chromic acid or permanganate, but when heated with the latter forms CO_2; it is very resistant to the action of reducing agents (sodium amalgam, etc.). The heat of combustion is 3700 Cals. (for 1 kilo).

MANUFACTURE OF ACETIC ACID. The most important prime material for the manufacture of crude acetic acid—from which salts are obtained for the preparation of the pure acid—is wood,[2] alcohol (from cereals and wine) being only rarely used. During

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[1] Oudeman's Table: specific gravity and concentration of acetic acid at 15°.

Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent. of acid by weight	Specific gravity	Per cent. of acid by weight
1·0007	1	1·0185	13	1·0412	30	1·0646	54	1·0748	78
1·0014	1·5	1·0192	13·5	1·0424	31	1·0653	55	1·0748	79
1·0022	2	1·0200	14	1·0436	32	1·0660	56	1·0748	80
1·0030	2·5	1·0207	14·5	1·0447	33	1·0666	57	1·0747	81
1·0037	3	1·0214	15	1·0459	34	1·0673	58	1·0746	82
1·0045	3·5	1·0221	15·5	1·0470	35	1·0679	59	1·0744	83
1·0052	4	1·0228	16	1·0481	36	1·0685	60	1·0742	84
1·0060	4·5	1·0235	16·5	1·0492	37	1·0691	61	1·0739	85
1·0067	5	1·0242	17	1·0502	38	1·0697	62	1·0736	86
1·0075	5·5	1·0249	17·5	1·0513	39	1·0702	63	1·0731	87
1·0083	6	1·0256	18	1·0523	40	1·0707	64	1·0726	88
1·0090	6·5	1·0263	18·5	1·0533	41	1·0712	65	1·0720	89
1·0098	7	1·0270	19	1·0543	42	1·0717	66	1·0713	90
1·0105	7·5	1·0277	19·5	1·0552	43	1·0721	67	1·0705	91
1·0113	8	1·0284	20	1·0562	44	1·0725	68	1·0696	92
1·0120	8·5	1·0298	21	1·0571	45	1·0729	69	1·0686	93
1·0127	9	1·0311	22	1·0580	46	1·0733	70	1·0674	94
1·0135	9·5	1·0324	23	1·0589	47	1·0737	71	1·0660	95
1·0142	10	1·0337	24	1·0598	48	1·0740	72	1·0644	96
1·0150	10·5	1·0350	25	1·0607	49	1·0742	73	1·0625	97
1·0157	11	1·0363	26	1·0615	50	1·0744	74	1·0604	98
1·0164	11·5	1·0375	27	1·0623	51	1·0746	75	1·0580	99
1·0171	12	1·0388	28	1·0631	52	1·0747	76	1·0553	100
1·0178	12·5	1·0400	29	1·0638	53	1·0748	77	—	—

[2] The wood of deciduous trees, after being dried at 110°, contains about 50 per cent. C, 6 per cent. H, and 44 per cent. O, its calorific value being about 4000 Cals.; air-dried wood, with 25 per cent. of moisture, gives about 2700 Cals.

The chemical change occurring in the decomposition of wood subjected to distillation at the recent years acetic acid has been manufactured synthetically from acetylene (*see later:* Acetic anhydride) similarly to the synthesis of alcohol (*q.v.*).

Dry Distillation of Wood. It has been already mentioned (*see* p. 38) that Lebon in 1799 patented a process of dry distillation of wood for producing illuminating gas and on p. 128, in dealing with the manufacture of methyl alcohol—also a product of the dry distillation of wood—the separation of the crude products of this distillation was described. A description will now be given of the apparatus used in this industry. It is not necessary to consider the primitive furnaces formerly used, which gave a minimal yield and a slow and incomplete carbonisation, or the vertical retorts used in the early days of the industry, although these are again in use nowadays, but in a far more rational manner. These first vertical retorts were followed by horizontal ones, which are still used in many factories.

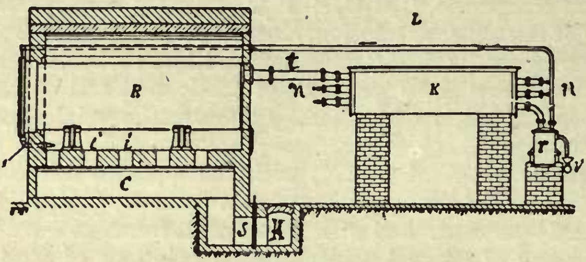

Fig. 233.

These are formed of sheet iron (10 to 12 mm. thick) and are about 1 metre in diameter and 3 metres in length; they are arranged in pairs in furnaces (Figs. 233, 234), with suitable flues for the hot gases, and they can be charged and discharged by means of a cover hinged at the back, although not very conveniently. On this account, and also in order to obtain continuous working, and hence more efficient utilisation of the heat of the furnaces, use is again being largely made of vertical retorts, which can be removed from the furnace at the end of the operation, to be replaced immediately by other retorts already charged. In Fig. 235, on the left, is seen the

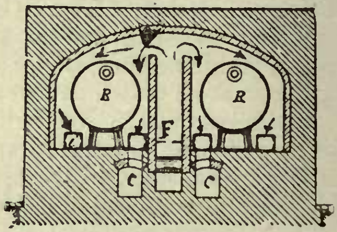

Fig. 234.

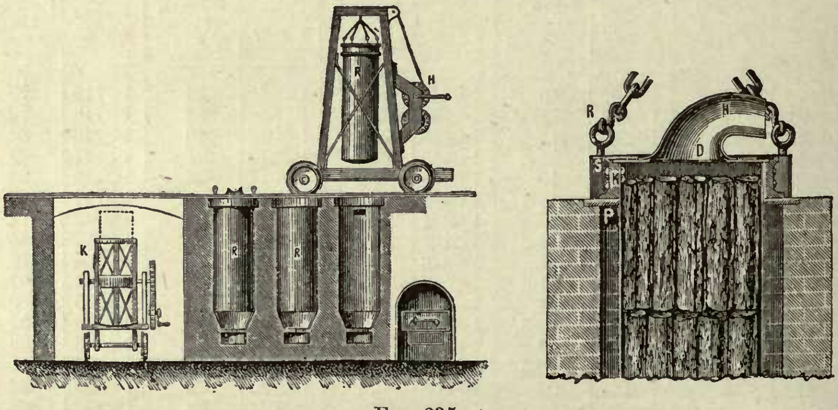

Fig. 235.

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ordinary pressure is represented by Klason (1914) by the following hypothetical equation, minimal empirical formulæ being ascribed to the wood, charcoal and tar, which are in good agreement with the elementary compositions of these products:

$$\underset{\text{Wood.}}{2C_{42}H_{56}O_{28}} = \underset{\text{Charcoal}}{2C_{16}H_{10}O_2} + 26H_2O + 5CO_2 + 3CO + 2CH_3\cdot CO_2H + CH_3\cdot OH + \underset{\text{Tar}}{C_{23}H_{18}O_4}.$$

Under practical conditions, however, less charcoal, less water and more gas are obtained than this equation indicates. Air-dried beech, containing 25 per cent. of moisture, yields on the average: 26 per cent. of dry charcoal, 5 per cent. of acetic acid, 1·5 per cent. of methyl alcohol, 8 to 9 per cent. of tar, 38 per cent. of water (25 per cent. from the moisture and 13 per cent. from the cellulose, etc., decomposed), and 20 per cent. of gas (*i. e.*, about 12 cu. metres per 100 kilos of wood).

arrangement of a battery of these retorts, with a trolley and crane *H* for raising and transporting the charged retorts, which are then emptied into the charcoal stove by means of the tipping trolley, *K*. The right-hand side of the figure shows in detail the upper part of a retort charged with wood. The capacity of each retort is about 4 cu. metres or 1500 kilos of wood; the smaller pieces are placed at the bottom, the medium-sized ones next, and the largest ones at the top. In order that the retorts may not be worn out too rapidly by the external heat, they are smeared with a very thin layer of earth made into a paste with water and applied with a brush. Every charge of 1500 kilos requires 600 to 800 kilos of coal for heating and distilling. If leaks are detected during the heating, they are closed with clay, and it is for this purpose that the retorts project 15 to 20 cm. beyond the furnace.

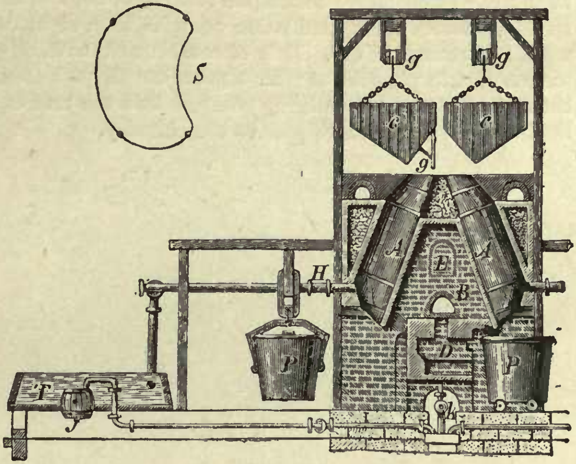

Fig. 236.

Although this arrangement is still largely used, it necessitates a considerable amount of manual labour and lifting, so that it has been proposed to incline the retorts as in gas-manufacture (*see* pp. 41, 43), and to furnish them with apertures at the top for charging and others at the bottom for automatically discharging them. Fig. 236 shows the section of a battery of these retorts (*A*) of the Mathieu type, *S* giving the cross-section of a retort. The wood is charged automatically from the running buckets, *c*, suspended at *g*. At the end of the operation the charcoal is discharged below into the vessel, *P*, which is provided with a cover to prevent the hot charcoal from igniting in the air. The vapours from the distillation pass into the tube, *H*, which conducts them into a coil cooled by the water in *T* and then into the barrel, *J*, where the tar and the pyroligneous acid separate; the gas, which does not condense, but is still partly combustible, is washed and passes through the pipe, *k*, to be burnt under the furnace-hearth, *D*; there is no danger of explosion, since, if there is any air in the retorts, it cannot communicate with the hearth, the barrel, *J*, serving as a water-seal.

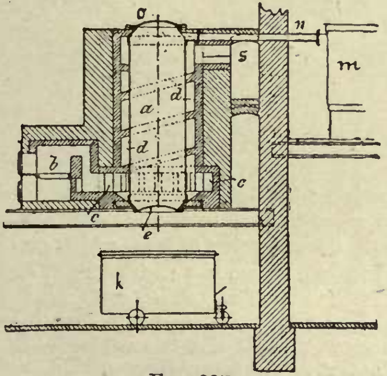

Fig. 237.

Of late years, use has also been made of vertical retorts (Fig. 237) with an upper orifice, *o*, for charging, and a lower one, *e*, for discharging (*see* Ger. Pat. 192,295, November 15, 1906). From the hearth, *b*, the hot gases pass to the flues surrounding the retort and thence at *S* to the shaft; the gases and vapours from the wood issue from the tube, *n*, and are partially condensed in the refrigerator, *m*. At the end of the distillation, the orifice, *e*, is opened and the charcoal discharged into the covered waggon, *k*, and conveyed to the store, whilst the retort, while still hot, is filled with a new charge of wood.

In order to diminish labour and other costs, use has been made for some years in the United States and in Sweden of very large retorts or furnaces. That shown in Fig. 238, which is most commonly used in America, consists of a furnace with parallelepipedal chambers, trolleys entering at one end charged with the wood and leaving at the opposite end with the charcoal. The distillation is continuous and in each furnace are two retorts *R*. The furnace with the flues which serve for the circulation of the hot gases from two opposite hearths, *F*, or from a single producer, and which surround the rectangular, thick sheet-iron retorts or chambers, resembles somewhat a metallurgical coke furnace (*see* Vol. I., p. 452). The wood is loaded in large waggons, *W*, which run on the rails *s*. The vapour and gas leave the retort by the tubes *T* connected with the condensers *V*, the non-condensed gas passing through the tubes *a* to the hearth; the arrows show the course of the hot gases in the vertical flues surrounding the retorts.

If the retorts are heated, not with wood and charcoal, but by the gases produced with hot air in a regenerator furnace (*see* Vol. I., pp. 487 and 634), one-third of the fuel is saved.[1] In small retorts every distillation occupies from eight to sixteen hours, according as the wood is seasoned or not. It is of considerable advantage to bark or split the wood and to season it in piles for at least a year, during part of the time protected from the rain; better still is it if before being charged into the retorts, the wood is dried or heated by the hot gases before these pass to the chimney.

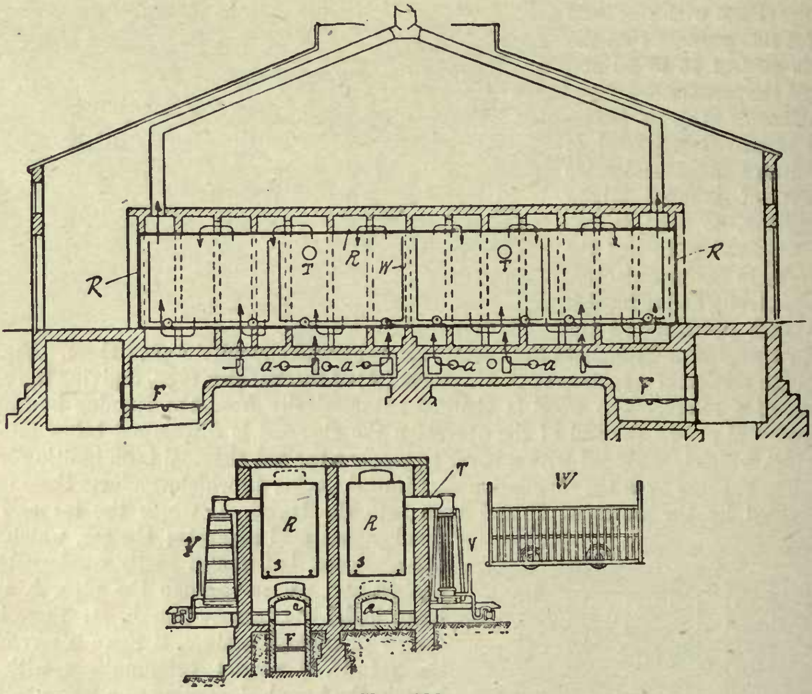

FIG. 238.

The yield of acetic acid and by-products varies widely with the kind of wood and with the conditions of distillation. Preference is usually given to hard woods like oak, hornbeam, and beech; of less value are white woods, with the exception of lime, which gives good results; the wood of trees eighteen to twenty years old, grown in a dry, poor soil and

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[1] That there is marked scope for saving fuel is shown also by the thermal balance derived from the chemical equation given in the note on p. 330. The reaction is exothermic, the theoretical positive heat being almost 6 per cent. of the heat of combustion of the wood. Hence, with a battery of furnaces in action, the amount of heat to be supplied for the distillation should be only that necessary to heat each fresh charge of wood to about 250° (at which the above exothermic reaction commences) and to evaporate the moisture of the wood, besides that carried off by the hot gases from the retorts and hearths and that of the hot charcoal extracted.

Since the non-condensable gases from the retorts (100 kilos of wood yield about 12 cu. metres containing, on the average, 56 per cent. of CO_2, 34 per cent. of CO, 8 per cent. of CH_4, and 2 per cent. of C_2H_4, and furnishing about 2000 cals. per cu. metre) are utilised for heating, and since also a good part of the heat of the hot gases from the flues and of the hot charcoal may be employed to dry or warm the wood prior to distillation, the quantity of wood burnt to heat the retorts should be only about 10 per cent. of that distilled. In most works, even those using seasoned wood, however, this proportion is as high as 30 to 35 per cent., and in only few cases is it below 20 per cent.

cut in winter, is more suitable than young wood or wood grown on plains in a moist or fertile soil and cut at other seasons of the year.[1]

UTILISATION OF THE SAWDUST. Many attempts have been made, not always successfully, to utilise the various forms of wood refuse, especially the sawdust. This presents, however, considerable difficulty, owing to the excessive moisture, the large volume, the abundance of resins which char and form incrustations, and the low thermal conductivity, which prevents the heat from reaching the middle of the retort.

The problem has not yet been definitely solved, but the forms of apparatus which up to the present have given the best results are that of Halliday (1851), shown in Fig. 239, and the more recent one of Rolle, used especially for distilling bituminous lignites (*see* p. 334) and shown in Fig. 240. Above the Halliday furnace the moist material (sawdust, exhausted dyewoods, etc.) is dried slowly in *a* and slowly descends a vertical screw moved by the cog-wheel, *b*, into the horizontal iron cylinder; there the mass is transported slowly to the opposite end by a horizontal screw and falls in a charred condition through the channel, *d*, into a water-tank, where it is extinguished. The vapours and gases from the distillation issue at *e* and *f* and pass to the condensing apparatus. The cylinder is heated by the hot fumes from the fire, *g*, several cylinders being heated at the same time in one furnace.

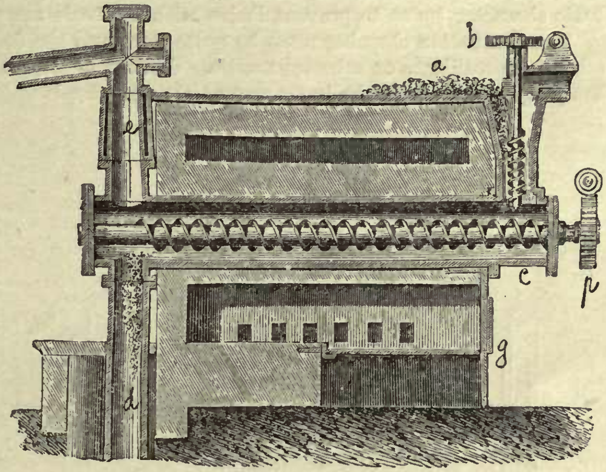

FIG. 239.

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[1] The yields obtained from 100 kilos of various kinds of wood, barked and subjected to rapid (*R*, about three hours) or slow distillation (*S*, more than six hours) are given below:

Kind of Wood	Tar	Aqueous acid distillate			Dry charcoal	Gas
		Total	Strength of acetic acid	Equal to pure acetic acid		
	Kilos	Kilos	Per cent.	Kilos	Kilos	Kilos.
Dogwood (*Rhamnus frangula*) branches . *S*	7·58	45·21	13·38	6·05	26·50	20·71
Do. Do. . . . . *R*	5·15	40·23	11·16	4·49	22·53	32·09
Hornbeam (*Carpinus betulus*) trunk . *S*	4·75	47·65	13·50	6·43	25·37	22·23
Do. Do. . . . . *R*	5·55	42·97	12·18	5·23	20·47	31·01
Alder (*Alnus glutinosa*) trunk . . *S*	6·39	44·14	13·08	5·77	31·56	17·91
Do. Do. . . . . *R*	7·06	40·70	10·14	4·13	21·11	31·13
Aspen (*Populus tremula*) trunk . . *S*	6·90	40·54	12·57	5·10	25·47	27·09
Do. Do. . . . . *R*	6·91	39·45	11·04	4·36	21·33	32·31
Birch (*Betula alba*) trunk . . . *S*	5·46	45·59	12·36	5·63	29·24	19·17
Do. Do. . . . . *R*	3·24	39·74	11·16	4·43	21·46	35·56
Beech (*Fagus sylvatica*) trunk . . *S*	5·85	39·45	11·37	5·21	26·69	21·66
Do. Do. . . . . *R*	4·90	45·08	9·78	3·86	21·90	33·75
Oak (*Quercus robur*) . . . . *S*	3·70	44·45	9·18	4·08	34·68	17·17
Do. Do. . . . . *R*	3·20	42·04	8·19	3·44	27·73	27·03
Austrian Pine (*Pinus laricio*) trunk . *S*	9·30	42·31	6·36	2·69	26·74	21·65
Do. Do. . . . . *R*	5·58	38·19	5·40	2·06	24·06	32·17
Pine (*Pinus abies*) trunk . . . *S*	5·93	40·99	5·61	2·30	25·55	28·11
Do. Do. . . . . *R*	6·20	40·15	4·44	1·78	23·35	32·80

A detailed study of the distillation of chestnut wood was made by G. Borghesani in 1910. The bark and branches always give a smaller yield.

The Rolle furnace has been applied in Germany on a vast scale to the distillation of brown, pitchy lignite and allows of continuous working and high output. It serves also for distilling small wood waste.

The furnace (Fig. 240) is 6 to 7 (or even 10) metres high and the inner cylindrical distillation chamber is about 1·7 metres in diameter. The outer masonry (shown with inclined shading) is of ordinary bricks, while the inner walls of the chamber and the flues *D* for the hot gases from the hearth *H* are of firebrick (dotted in the figure) of distinctly basic character (so as to prevent fusion with the basic ash carried over by the gases).

The distillation chamber must be quite tight and the firebricks are fitted one into the other with a silicate or asbestos mastic. Contact of the material to be distilled with the hot peripheral walls of the inner part of the chamber is ensured by inserting a column of truncated conical rings of siliceous cast-iron or enamelled iron, these being superposed and kept in position by a central vertical rod joined by transverse rods to certain of the rings; the uppermost conical ring is provided with a cover. The wood waste is charged peripherally at the top and gradually chars as it passes automatically to the bottom, where it collects in the hopper *F* and is discharged periodically, by opening *G*, into the iron truck underneath, this being at once covered to prevent ignition of the charcoal.

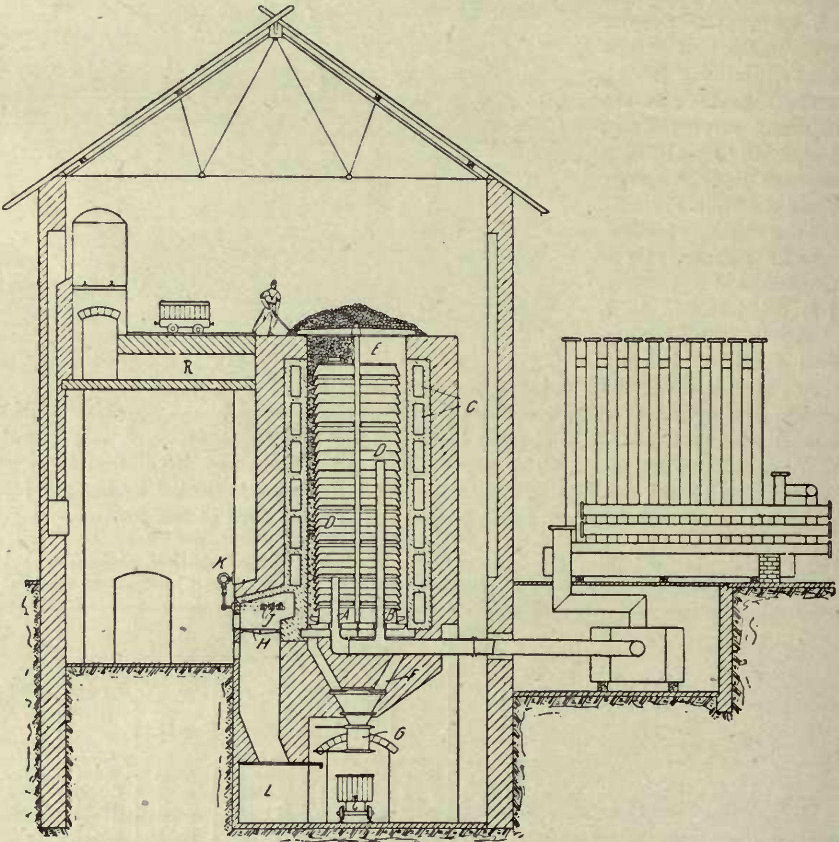

FIG. 240.

The gases and vapours produced pass between the rings into the inner space, from which they are drawn through the tubes *A* and *B* to the external condensation apparatus. The non-condensed gases are led through *K* to the distributor *I* in the hearth *H*, where they are burnt together with charcoal and wood, the combusted gases passing through the flue *R* to the chimney; these non-condensed gases are sent to the hearth only when the walls of the furnace are already very hot, since otherwise they extinguish the fire. Use of the gases in this way saves more than one-half of the fuel, 30 kilos (instead of 80 to 100 kilos) of the latter being then sufficient for the distillation of 100 kilos of wood. With large furnaces the heating may be effected solely with gas (obtained partly from producers). These chamber retorts are 15 to 18 metres in length and contain four or five trucks, each holding 6 to 8 cu. metres of wood.

F. H. Meyer obtains better results by using two large retorts or cylinders set horizontally in a furnace. Into these cylinders run trolleys carrying metal plates with the sawdust spread out in thin layers. The fire is started and the first cylinder heated and distilled rapidly, the hot fumes then going to heat the second cylinder and so dry the sawdust, which is made ready for distillation, whilst the first cylinder is discharged and again charged with fresh sawdust. In Russia and America, large quantities of resinous woods are distilled, and these yield considerable amounts of resins and oils (of pine, turpentine, etc.) if superheated steam is used.

A large works was started at Cassel in 1900 to distil sawdust according to the Bergmann patents, the sawdust being strongly compressed into bricks with the hope of expressing the moisture and obtaining compact charcoal; neither of these ends was attained and the works failed. Similar to this is the Heidenstam process, according to which the charcoal is pressed also during its formation or distillation. Bühler (1902) dries the sawdust with the hot flue gases and then carbonises it, the powdered charcoal being pressed with tar and fresh sawdust into blocks, which are afterwards heated in a charcoal furnace to char the sawdust and tar, and to obtain bricks of light wood charcoal; the volatile products of this second distillation are also recovered.[1]

In 1905 the suggestion was made to distil wood in retorts in a current of chlorine so as to obtain acetic and hydrochloric (70 per cent. of the chlorine used) acids at the same time, but grave difficulties were encountered in obtaining a material resistant to these acids. Further, Larsen constructed rotary furnaces for the distillation of wood, and in 1904 an attempt was again made in Sweden to distil resinous woods with superheated steam so as to obtain an increased yield of turpentine.

The *liquid products* from the dry distillation of wood are condensed in cooling coils and collected in large wooden vats. They consist mostly of an aqueous solution of acetic acid (*see* Table in preceding note), methyl alcohol (about 1 per cent.), and acetone (nearly 0·1 per cent.), and of small quantities of other acids (formic, propionic, butyric, valeric, caproic, etc.). On this liquid floats part of the tar, the rest of which collects at the bottom; the tar may be easily separated by decantation or by means of a centrifuge—such as is used for the separation of cream from milk—a low temperature and sometimes addition of a little tannin being used to facilitate the separation.[2] The aqueous solution, which is brown, and has an unpleasant odour owing to the presence of empyreumatic products, may be treated in various ways according as crude acid or a purer acid is required. In the first case it is filtered through wood-charcoal, left to stand for a week to see if any further tar separates, and then distilled fractionally from a large copper still; the methyl alcohol and acetone are first collected (at 60° to 70°) and then the crude *pyroligneous acid* (beyond 95°), which has a strong empyreumatic odour, turns brown rapidly in the air and contains 6 to 8 per cent. of acetic acid.

None of the attempts made to purify and deodorise this product have given satisfactory results and to obtain a less impure acetic acid, calcium acetate is first formed and from this the acetic acid recovered (*see later*).

The separation of the various components of the crude pyroligneous acid and the simultaneous preparation of *calcium acetate* is usually effected by a process in which three boilers are employed (Fig. 241). The crude, decanted pyroligneous acid is pumped into the large vat, *A*, from which it passes to the copper boiler, B_1 (3000 to 5000 litres), where it is boiled by means of steam-pipes (steam entering at V under 3 to 4 atmos. pressure and the condensed steam issuing at S). The vapours of acetic acid, methyl alcohol and acetone are passed through the tube, *t*, to the bottom of the second boiler, B_2 (1000 to

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[1] Sawdust from the wood of the Coniferæ (resinous) is not suitable for distillation, as it gives lower yields of charcoal, acetic acid and methyl alcohol than that of deciduous trees, especially of hard woods; further such sawdust contains scarcely any of the valuable pine oil and the tar is of little value.

[2] The *tar* is washed with water and heated to recover the acetic acid it contains, the tar thus obtained free from acid being used in the manufacture of rubber and of electric cables, its price being 4*s*. to 5*s*. per cwt.

2000 litres), filled with milk of lime (from the lime-tank, *L*), which soon becomes heated nearly to boiling but retains the greater part of the acetic acid as calcium acetate, whilst the vapours proceed through the boiler, B_3, which also contains milk of lime; finally, the methyl alcohol and acetone vapours are condensed in the cooler, B_4, and collected in the rèservoir, *D*, after passing through the test-glass, *m*, which indicates the density (*see* Fig. 131, *E*, p. 160, and Fig. 134, *E*, p. 161). The distillation goes on until the density reaches the value 1·00, this usually occurring when one-third or one-quarter of the total liquid of the boiler, B_1, is distilled. The first methyl alcoholic liquid which condenses, being more concentrated (30 to 40 per cent.), is kept and rectified apart from the remaining more dilute liquid by means of an ordinary rectifying column, H_1, H_2, H_3, in Fig. 241 (*see also* Fig. 140, p. 165).

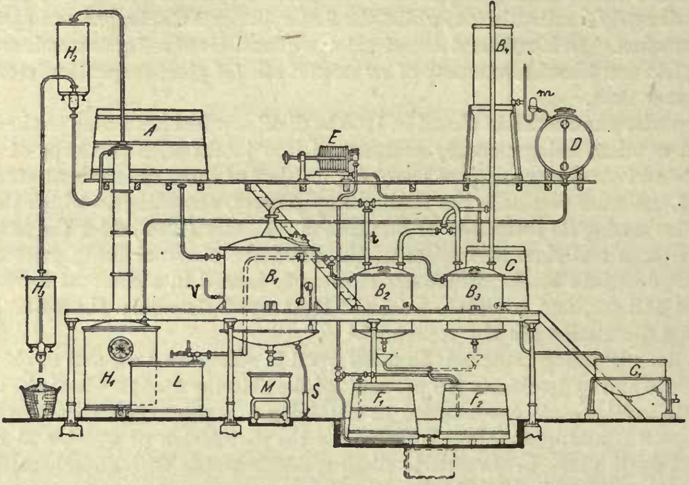

FIG. 241.

The aqueous tarry residue left in B_1, after evaporation of all the acetic acid, is discharged into the movable tank, *M*.

When the liquid in the second boiler, B_2, assumes an acid reaction, the vapour from B_1 is passed into B_3, whilst B_2 is discharged into the vat, F_1, below, and again filled with milk of lime, into which the vapours from B_3 pass before they proceed to the condenser, B_4; a similar change is then made when the contents of B_3 become acid, and so on. The calcium acetate (about 20 per cent.) is pumped to the filter-press, *E*, and the clarified solution collected in the vat, *C*, which feeds the evaporating pans (iron or copper) fitted at the bottom with a lens-shaped jacket, C_1. This is best seen in Fig. 242: the steam for heating is passed in at *a* and the condensed steam runs off at *b*; *f* is a hood fitted with counter-weights, *g*, and hence capable of being raised, its object being to carry off the irritating acid vapours rising from the pan. More effective are pans with double concave bottoms. The concentration readily attains a value of 40 per cent.; the liquid then becomes pasty and must be stirred, this being continued until the mass will crumble between the fingers. The acetate is then lightly roasted at 125° to 145° on iron or copper plates heated by the hot gases from the pans or from the furnaces used for distilling the wood. By this means the mass loses the residual water and certain volatile tarry and empyreumatic products retained by the mass, which changes from brown to grey, if it is kept well mixed until it can be powdered between the fingers. For this roasting use is also made of continuous furnaces similar to the Hasenclever apparatus for making calcium hypochlorite (*see* Vol. I., p. 624), steam at about 200° being passed in at the bottom of the apparatus instead of chlorine. In this way a product containing up to 80 to 82 per cent. of *calcium acetate* is obtained. According to U.S. Pat. 927,135 (1909) white calcium acetate of very

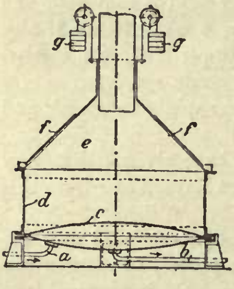

FIG. 242.

high purity (86 to 92 per cent.) is obtained if the concentration and drying are carried out in a vacuum. The product is then broken up somewhat, and sold in bags holding 60 to 70 kilos. It contains 80 to 84 per cent. of pure calcium acetate,[1] 10 to 12 per cent. of water (half of which is lost only at about 150°), and 6 to 7 per cent. of impurities ($CaCO_3$, CaO, tarry matters, etc.).

F. H. Meyer (Ger. Pat. 214,558, 1908) obtains calcium acetate free from phenolic compounds (which calcium acetate usually holds very tenaciously in the form of an emulsion) by passing the gases from the distillation of the wood—when freed from tar—into a tower containing lumps of calcium carbonate, which combines with the acetic acid but not with the phenols.

Also the fractional condensation method described in U.S. Pat. 969,635, 1910 (I. Heckel), although somewhat complicated, represents a marked improvement.

To obtain acetic acid from calcium acetate, the latter was formerly decomposed with hydrochloric acid. Nowadays, however, the decomposition is effected with concentrated sulphuric acid, the substances being mixed slowly in shallow iron pans arranged over a furnace and fitted with covers and stirrers: for 100 kilos of calcium acetate, 65 to 70 kilos of commercial sulphuric acid of 66° Bé. In order to avoid the formation of sulphur dioxide and other decomposition products at the high temperature attained initially and prevailing during the distillation, K. Linde distils in a vacuum with steam-heat (superheated if necessary); this procedure renders the operation more rapid and the acetic acid purer, besides reducing the consumption of sulphuric acid almost to the theoretical amount (60 kilos) and allowing of the treatment of larger quantities of material at a time; further, the final portions of acetic acid, which are retained with great tenacity by the calcium sulphate, may be more easily and completely separated. The left-hand half of Fig. 243 shows diagrammatically the arrangement used in treating calcium acetate, when vacuum distillation is not employed. The sacks of calcium acetate, *a*, on the upper floor are tipped through a hopper on to the flat cast-iron pans, *b*, fitted with stirrers; the pans are then closed and the measured amount of sulphuric acid in *n* (supplied from the large leaden tanks, *e*), slowly introduced. The mass, which begins to heat, is then heated by the fire underneath, the stirrers being kept in motion meanwhile.

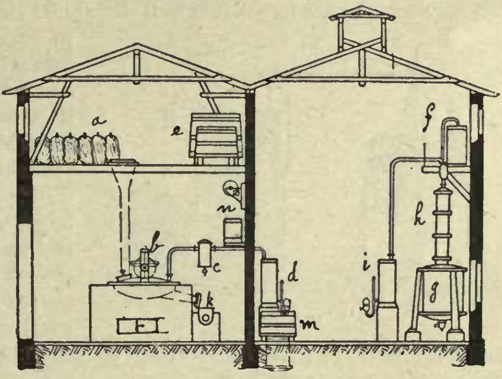

FIG. 243.

The acetic acid is gradually evolved from the copper tube leading first to the vessel, *c*, where the powder and acid spray carried over are deposited, and then to the copper coils in *d*, where the acetic acid is condensed and cooled, to be collected in the tank, *m*; a lateral test-glass, containing an aerometer, is fitted to the condenser and allows the density of the distilled acid to be read off at any moment. When the vapour-delivery tube begins to cool, the operation is at an end; the fire is then covered with ashes and the residual calcium sulphate discharged through a wide lateral tube, *k*, and conveyed from the factory by an archimedean screw. Another distillation is then immediately commenced.

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[1] The *strength of commercial calcium acetate* is determined by introducing a homogeneous sample of 5 grams into a distilling flask with 50 c.c. of water and 50 c.c. of pure phosphoric acid (sp. gr. 1·2); the mixture is shaken and heated gently to avoid frothing, the distillation products being cooled and condensed. When the residue becomes dense, the distillation is continued in a current of steam. The distillation is continued until the distillate amounts to about 200 c.c.; this is then made up to 250 c.c. Part of this liquid is tested for hydrochloric and phosphoric acids and 50 c.c. of it is titrated with normal caustic soda solution with phenolphthalein as indicator to determine the amount of acetic acid; 1 c.c. of the normal soda solution corresponds with 0·079 gram of calcium acetate. This titration also gives, besides acetic acid, traces of other volatile acids contaminating the calcium acetate, but this error is inevitable. Aqueous solutions of pure calcium acetate have the following densities: 5 per cent., 1·0330; 10 per cent., 1·0492; 15 per cent., 1·0666; 20 per cent., 1·0874; 25 per cent., 1·1130; 30 per cent., 1·1426.

The yield from 100 kilos of calcium acetate amounts, under favourable conditions, to 80 kilos of 72 to 75 per cent. acetic acid, which always contains a few per cent. of sulphurous acid. Part of the latter has been already eliminated during the distillation as uncondensed gas and carried to the chimney. During recent years the introduction of vacuum distillation has been almost universal, as it economises fuel, gives an increased yield and a purer product, and accelerates complete distillation with a minimal production of sulphurous acid.

It will be readily understood that the use of less concentrated sulphuric acid and moist calcium acetate gives a more dilute acetic acid. A large part of the acetic acid is put on the market as it is or diluted with water to bring it to a concentration of 40 per cent., which is often required practically.

When, however, purer and more concentrated acid is desired, use is made of a rectifying column quite similar to those employed in the case of alcohol (*see* p. 165). The column is, however, constructed of copper, as this metal is more resistant (although not completely so) than others towards organic acids, if air is excluded. The heating is carried out with indirect steam under 5 atmos. pressure, which circulates in coils at the bottom of the still. The copper column is fitted inside with perforated plates of porcelain or baked clay arranged alternately with copper or clay rings; the condenser consists of a copper, or, more rarely, a clay coil. The right-hand half of Fig. 243 represents the rectifying apparatus: *g* is the still, *h* the column, *f* the dephlegmator, and *i* the condenser. When the apparatus is not in use it is well rinsed and then completely filled with water, in order to prevent the acid, in presence of air, from attacking the copper. The first portion (about one-fourth) of the distillate is kept separate, as it is more dilute and contains the sulphurous anhydride and a large part of the empyreumatic products, and the last tenth or more is not distilled, but is also kept separate, being very impure. According as more or less foreshots and tailings are separated, a very concentrated (96 to 99 per cent.) acid, or one of about 80 per cent. strength is obtained, both, however, containing traces of copper and empyreumatic products; the latter may be removed by mixing the acid in clay vessels with a little concentrated potassium permanganate and then filtering. The empyreumatic substances may also be removed (*e. g.*, in the manufacture of essence of vinegar) by distilling the acid over potassium chromate. Traces of copper are eliminated by redistilling this acid from a copper still by means of indirect steam, the condensing coils and tubes being of earthenware or silver and carboys being used for collecting the pure, refined acid. Nowadays it is sometimes considered preferable to construct the small head of the still and the whole of the refrigerating coil of silver, as is shown in Fig. 244, since the coil then conducts heat well and is not much more expensive than the two earthenware coils necessary to give the same rapidity of condensation; besides which, earthenware coils are fragile and of no value when broken.[1] According to Ger. Pat. 220,705, 1907, pure acetic acid containing only traces of SO_2 may be obtained by heating calcium acetate (100 parts) to 130° in a vacuum and then introducing a mixture (55 parts) of equal amounts of acetic and concentrated sulphuric acids; by continuing the heating in a vacuum, the whole of the acetic acid, including that added, distils over, the yield being 95 per cent.

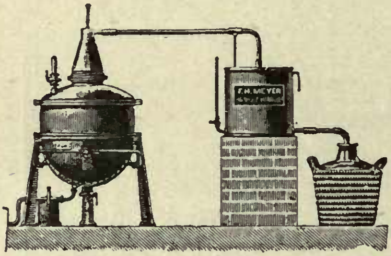

FIG. 244.

During the winter care must be taken not to cool the condensing coils too much, as otherwise the pure (glacial) acetic acid may solidify and cause obstruction. Also in stores where acetic acid is kept in wooden casks, earthenware vessels, or carboys, the temperature

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[1] *Testing of acetic acid.* If no empyreumatic products are present, a mixture of 10 c.c. of the acid, 15 c.c. of water, and 1 c.c. of 0·1 per cent. potassium permanganate solution will remain reddish in colour for more than one minute. The acid should not contain higher homologous acids; these are detected by dissolving PbO (litharge) in the 30 per cent. acid until only a faint acidity remains, the solution being then heated and filtered; if the crystals which form are not transparent and colourless, but show white flocks like mould, the acid is to be rejected. The presence of other organic acids in acetic acid may also be detected by fractionally precipitating the silver salt and determining the silver in the separate fractions by heating in a crucible. Pure silver acetate contains 64·6 per cent. of silver. For other tests *see* note on p. 340.

must be maintained above 16° if troublesome solidification of large quantities of the acid is to be avoided. *Glacial acetic acid* is also prepared by distilling 92 parts of pure dehydrated (by fusion at 240°) sodium acetate with 98 parts of concentrated sulphuric acid. In 1901, the Rhenania chemical firm patented a process for distilling calcium acetate with a sodium polysulphate, $NaH_3(SO_4)_2$, which acts like sulphuric acid but without giving secondary decomposition products. Formerly, *glacial acetic acid* was obtained by *Melsen's reaction* (1844), which consists in adding potassium acetate to dilute acetic acid and evaporating until a salt, combined with acetic acid, crystallises; this salt, which melts at 148°, decomposes at 200° to 250°, pure glacial acetic acid distilling and the potassium acetate (which decomposes only above 300°) remaining for a subsequent operation.

SYNTHETIC ACETIC ACID FROM CALCIUM CARBIDE. This process was described on p. 171, in the chapter on synthetic alcohol. In a works erected by the Società Italiana Prodotti Sintetici (SIPS) to make use of the Lonza process, the oxidation of the acetaldehyde formed as an intermediate product (*see* p. 171) is to be effected by means of oxygen from liquid air. The economical synthetic manufacture of acetic anhydride seems assured, and glacial acetic acid will probably be obtained with the help of the dilute acetic acid produced by the older processes.

USES OF ACETIC ACID. Considerable quantities of commercial acetic acid (35 to 40 per cent.) are used in printing and dyeing wool and silk, especially with alizarin and other dyes which withstand feebly acid baths; it is also largely employed for giving silk its characteristic rustling property after dyeing or cleaning. The pure acid serves in the preparation of numerous acetates (ammonium, chromium, and aluminium—which are used in dyeing fabrics and rendering them impervious—lead, etc.), different esters and various aniline dyes. After it became obtainable in a pure state by rectification, it acquired great importance for the preparation of essence of vinegar (various aromatic herbs being added) and, when diluted with water, replaces ordinary table vinegar.

Glacial acetic acid serves also to separate the *paraffin wax* from lignite and petroleum tars (*see* pp. 94 and 97). According to Tanne and Oberländer (Ger. Pats. 226,136 and 227,334, 1909), 100 kilos of petroleum residues is treated in the hot with 45 kilos of benzine and 5 kilos of glacial acetic acid, the liquid being decanted off and cooled slowly for twelve hours; the dishes containing the solution are then kept in a refrigerating chamber below 0°, the paraffin wax separating being finally removed by means of hydraulic presses.

It has been proposed to denature acetic acid, to be used in chemical industries, by addition of formic acid, so that it may be freed from taxation (in Italy).

STATISTICS OF ACETIC ACID AND CALCIUM ACETATE. Before the European war but little calcium acetate was produced in Italy, but large quantities of calcium acetate were imported from the United States (import duty 8*s*. per ton) and treated; this importation amounted to :

	1903	1905	1910	1913	1914	1915	1916	1917	1918
Tons .	407	1,625	1,320	2,326	2,023	2,604	2,168	2,891	847
Value, £ .	—	12,654	13,199	27,314	21,040	63,300	130,080	208,200	61,000

Large amounts of acetic acid of various strengths are also imported into Italy.[1]

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[1] The manufacture of crude pyroligneous acid in Italy is exempt from taxation, but the rectification and production of the pure acid are subject to a manufacturing tax of 12*s*. per quintal (of pure acid) for acid of less than 10 per cent. strength; 41*s*. for 10 to 30 per cent. acid; 72*s*. for 30 to 50 per cent. acid; 100*s*. for 50 to 70 per cent. acid; 129*s*. for 70 to 90 per cent. acid; and 144*s*. for stronger acid. The Customs import tariff adds a further tax of from 19*d*. to 17*s*. 6*d*. according to the strength. The production of pure dilute acetic acid for artificial vinegar is usually effected by the oxidation of alcohol, which is supplied almost free from the alcohol tax, although the acetic acid tax remains.

For Germany the importation and exportation are as follows (tons):

	1905	1908	1910	1911	1912	1913
Calcium acetate imported . .	20,500	17,394	17,860	20,408	21,690	20,920
Glacial acetic acid or anhydride exported	—	1,200	1,570	1,490	1,774	1,597

The calcium acetate is imported principally from the United States and partly also from Austria. In Germany itself more than 16,000 tons of the acetate are made annually. In 1910 Germany imported 4800 tons of dilute pyroligneous acid (less than 30 per cent. strength) for purification.

The output of calcium acetate in the United States[1] was 400,000 tons in 1900 and about 800,000 tons in 1914, one-half being exported (360,000 tons in 1911). The *acetic acid* consumed in the United States amounted to 14,000 tons in 1900 and 13,500 tons in 1905, 14 per cent. being used in making dyes, 3 per cent. for lead acetate, 25 per cent. in paper-making, 45 per cent. in the textile industries (dyeing), 14 per cent. for making white lead, and 9 per cent. for other purposes.

In 1910 the wood from 200,000 hectares (490,000 acres) of forest was distilled in France, various products of the value £600,000 being obtained. The amounts of calcium acetate imported and exported were as follows (tons):

	1913	1914	1915	1916
Importation . .	180	969	498	790
Exportation . .	315	41	729	60

Great Britain imported 3500 tons of calcium acetate in 1909 and 4300 tons (£86,400) in 1910.

In 1909 Brazil imported acetic acid to the value of £120,000.

The price of the acid varies with the purity and concentration; ordinary commercial 30 per cent. (sp. gr. 1·041) was sold before the war at about 12*s.*; the 40 per cent. acid (sp. gr. 1·052) at 15*s.* to 16*s.*; and the 50 per cent. acid (sp. gr. 1·061) at 20*s.* per cwt. The pure acid costs 25 per cent. more than the commercial at the same concentration, and the pure glacial (99 to 100 per cent.) 44*s.* to 46*s.* per cwt.[2]

MANUFACTURE OF VINEGAR

Vinegar is formed by the acetic fermentation (by means of *Mycoderma aceti*, *Bacillus aceticus*, or *Bacterium aceti*, *see* p. 145, Fig. 116, *a*) of saccharine liquids which have undergone alcoholic fermentation, such as wine, beer, cider, etc. Since this transformation of alcohol into acetic acid takes place merely on exposure of these liquids to the air, it is

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[1] In the United States the distillation of wood has been organised, both technically and commercially, as a large modern industry, all the works being combined to a syndicate, which regulates the trade in calcium acetate with the whole world. In 1900 1,767,380 cu. metres of wood were distilled and in 1907 about 4,391,000 cu. metres (only 10 per cent. of resinous wood) in 100 distilleries, the mean yield being 0·5 cu. metre of charcoal, 8 to 10 litres of 82 per cent. methyl alcohol, 22 to 25 kilos of 80 to 82 per cent. calcium acetate, and 15 to 20 litres of tar per cu. metre of wood, and with a consumption of 0·6 cu. metre of wood for heating the retorts, stills and other plant. One-half of the output of the United States is supplied by Michigan and one-fourth by Pennsylvania.

In Canada there are wood-distilling works at Quebec, Ontario and Montreal, where also products from other factories are treated. Altogether 2300 workpeople are employed, the annual output being 80,000 tons of wood charcoal, of the value £120,000, 14,000 tons of calcium acetate, of the value £100,000, 400 tons of acetone, worth £240,000, and 1400 casks of formaldehyde, worth £100,000.

[2] **Testing of Acetic Acid.** Better than by the specific gravity the strength is determined by titrating a *weighed* quantity of the acid with normal caustic soda solution (1 c.c. = 0·06004 gram of acetic acid) in presence of phenolphthalein. When the acid contains more than 2 per cent. of water it no longer dissolves cedarwood oil or oil of turpentine. Metallic impurities are detected by diluting 10 c.c. to 100 c.c., neutralising with ammonia and adding ammonium sulphide and then ammonium oxalate: the pure acid should show no alteration or precipitate. If sulphuric acid is absent, the acid, diluted with 10 volumes of water and treated in the hot with barium chloride, gives no precipitate even on standing for some hours. In absence of hydrochloric acid, dilution and addition of nitric acid and silver nitrate produces no turbidity. Absence of empyreumatic products is shown by mixing 5 c.c. of the acid with 15 c.c. of water and 5 c.c. of centinormal permanganate solution: the liquid should not become decolorised in fifteen minutes. For the detection of other organic acids in acetic acid and other tests, *see* notes on pp. 338 and 344.

probable that vinegar and hence acetic acid was the first acid known to man. The same result is obtained by treating alcohol with various oxidising agents (chromic acid, ozone, manganese dioxide and sulphuric acid, etc.), but acetaldehyde is also largely formed in these cases, which hence do not compete in practice with the biological process. The composition of vinegar was studied by Berzelius (1814), and Kützing in 1837 showed the importance of the living organism of the mother-of-vinegar to the formation of acetic acid, while Turpin in 1840 examined and characterised these micro-organisms more exactly. According to Liebig, the transformation of alcohol into acetic acid is brought about by the catalytic action of certain nitrogenous substances capable of fixing oxygen from the air and of yielding it to the alcohol. In 1868, however, Pasteur showed that this phenomenon is caused by a vegetable organism, *Mycoderma aceti*, formed of small, oblong cells (about 3 micro-mm. long), slightly constricted in the middle (where segmentation then takes place) and often arranged in chains. When these multiply at the surface of the alcoholic liquid, they form first a thin membrane which gradually thickens, and when this membrane is formed in the body of the liquid it becomes mucilaginous and spreads through the whole liquid, giving a compact mass—the so-called *mother-of-vinegar*—reaching to the surface. It develops very well in slightly alcoholic liquids (3 to 6 per cent., but better with 13 per cent. of alcohol, and still more readily in presence of about 1 per cent. of acetic acid and 0·1 per cent. of phosphate); the most favourable temperature is about 30°, acetification ceasing at 45° or below 5°; the action is retarded by light. When the acetic membrane becomes submerged, the fermentation ceases and only recommences with the formation of a fresh superficial membrane, which can absorb oxygen from the air and transfer it to the alcohol:[1]

$$CH_3 \cdot CH_2 \cdot OH + O_2 = H_2O + CH_3 \cdot COOH.$$

According to this equation, the theoretical yield is 60 grams of acetic acid per 46 grams of alcohol, but the practical yield is 15 to 20 per cent. less than this; under the most favourable conditions, a liquid containing 10 per cent. of alcohol by *volume* yields a vinegar with 10 per cent. of the acid by *weight*. When almost all of the alcohol is converted into acetic acid, part of the latter begins to decompose into $H_2O + CO_2$; this change may be avoided by continuing to add alcohol to the acetic liquid or by causing the mother-of-vinegar to sink, and decanting the liquid. The old or slow wine vinegar process, known as the *Orleans process*,[2] has been replaced almost everywhere by the more rapid *German*

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[1] This explains the harmful effect of *vinegar worms* (small worms belonging to the Nematodes), which form a transparent, white, slimy mass moving along the walls of the vessel, and breaking the skin of *Mycoderma aceti* at the surface of the liquid and hence causing it to sink. Another enemy of vinegar is the *vinegar mite* (an insect $\frac{1}{4}$ mm. in length), which multiplies at an enormous rate and accumulates in large masses in the vinegar, succeeding in interrupting the acetic fermentation and starting putrefactive changes. In order to prevent the entry of these insects into the vats and casks, the latter are smeared outside with a ring of birdlime, to which the mites become fixed. Direct sunlight also hinders the development of the worms. Also *Mycoderma vini* hinders the development of *Mycoderma aceti*, and equally harmful to acetic fermentation are antiseptic substances in general, sulphur dioxide and empyreumatic substances (including those of pyroligneous acid). Blue and violet light (hence white light, but not red or yellow light) likewise retard the growth of *Mycoderma aceti*.

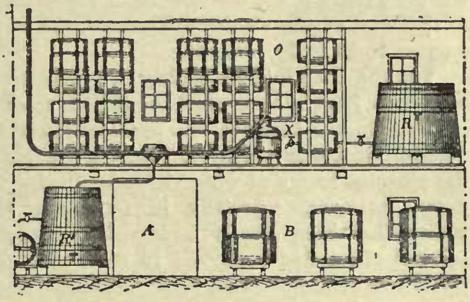

FIG. 245.

[2] This process is one of the oldest, and was formerly, and is still, carried out more especially in the town of Orleans, by filling a number of superposed casks (Fig. 245) to the extent of one-eighth of their volume with good wine vinegar and then adding each week about 10 litres of wine (or wine-dregs, containing 8 to 10 per cent. of alcohol, filtered through beech shavings in the vat, *R*; white wines are preferable). When the casks are about half-full, the vinegar is made, and two-thirds of it is drawn off and either filtered through beech chips or allowed to deposit in the vat, *R'*, underneath; the addition of 10 litres of wine per week is then continued. By means of the stove, *X*, the temperature is maintained at 25° to 30°. This method gives a fine, aromatic vinegar, but it is very slow and cannot be interrupted when desired. Pasteur prepared vinegar of an inferior quality more rapidly by adding a little vinegar to wine in wide, shallow vats and then sowing on the surface a little pure *Mycoderma aceti* from another vat.

process, proposed by Schützenbach in 1823 and subsequently greatly improved. As early as 1730, however, Boerhave prepared vinegar—and in some places his method is used even to-day—by means of two vats standing on feet and communicating at the bottom by means of a tube. One vat is filled with the wine, but the other is only about half filled, the vinasse not being submerged. Every twelve hours the full vat is half emptied into the other. If the temperature is kept at 25° to 30°, acetification is complete in 12 to 15 days.

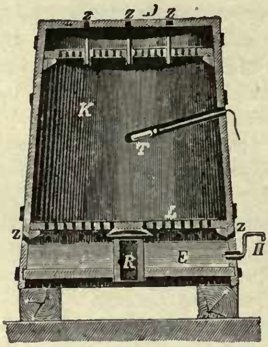

FIG. 246.

In the German or *quick vinegar process*, wooden vats, 2·5 to 3 metres high and 1·5 to 2 metres in diameter, are used (Fig. 246). These are filled almost completely with beech shavings, which are supported on a perforated false bottom, *L*, and covered with a wooden disc with perforations traversed by cords held by knots so as to form a uniform spray of the alcoholic liquid (8 to 10 per cent.), mixed with one-fifth of its volume of wine vinegar, over the wood chips. Six or seven glass tubes passing through the upper disc allow of a continuous circulation of air, which enters at the periphery of the lower part of the vat through the holes, *Z*, and through the pipe, *R*, passes through the shavings—which become gradually warmed as acetification proceeds—and issues through the apertures, *Z′*, at the top. The temperature is shown by a thermometer, *T*, inserted in a glass tube, reaching to the middle of the vat. When the temperature exceeds 40°, it is lowered by a more rapid passage of the alcoholic liquid, which collects at *E* and is discharged by the siphon, *H*, to be conveyed to the top of the vat and again circulated through the shavings, this process being continued until acetification is complete. In some cases three such vats are superposed, the liquid passing down through them all; after one or two complete circulations the operation is complete, although the amount of acid formed is not equal to that of the alcohol in the original liquid.

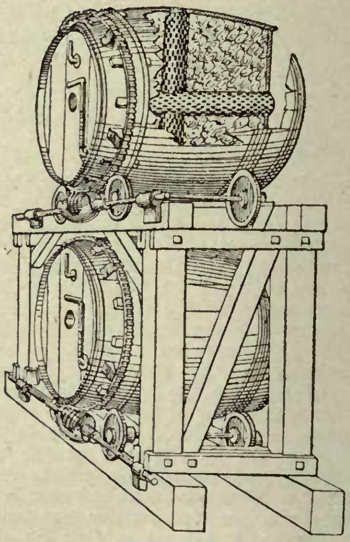

FIG. 247.

The liquids thus obtained contain up to 12 to 13 per cent. of acetic acid (14 per cent. cannot be exceeded, as the *Mycoderma* would then be killed) and, if the operations are conducted with care, less than 10 per cent. of the alcohol used is lost; otherwise, especially if the temperature becomes too high, so that part of the alcohol evaporates, the loss may amount to 30 to 50 per cent.

Vinegar of an inferior quality is largely prepared nowadays from various alcoholic liquids made from cereals, starch, beetroot, or molasses, just as industrial alcohol is prepared, but such vinegar lacks the pleasant aroma of wine vinegar. During recent years, however, especially in Germany, alcohol vinegar has been greatly improved by using pure cultures of selected bacteria. In 1912, about 30,000 hectolitres of alcohol were converted into vinegar in Austria and 150,000 in Germany.

It has been proposed to accelerate acetification by means of compressed air, but greater success has attended the *Michaelis* or *Luxemburg method*, in which acetification is carried out in rotating casks (5 to 6 hectolitres) filled with beech shavings (washed first with hot water and then with hot vinegar) and traversed by two osier tubes, one along the horizontal axis and the other along the vertical axis, to allow of the circulation of air. The shavings are washed with wine vinegar, and the cask about half filled with wine (Fig. 247). During the first three days the casks are rotated three times a day and subsequently six times a day. Acetification is complete in about eight days.

An ingenious, rapid, and continuous method for the manufacture of vinegar is that of Villon (Fig. 248), which makes use of two drums (2 metres by 2 metres), *B B*, arranged inside in the form of a spiral. The iron spirals are covered or varnished with gutta-percha, and are 30 metres in length, the coils being 10 cm. apart and the spaces between filled with beech shavings (washed with HCl) or charcoal. The drums rotate in opposite directions, the left-hand one rotating once in five minutes and dipping up each time 8 litres of the alcoholic liquid from the vessel, *C*, this liquid being then passed through the axial tube to the second drum, which discharges it into the other dish, *C*. The liquid then passes to a similar pair of drums and thence to a third pair, on leaving which the vinegar is ready; by this means 1000 litres are produced in twenty hours. By means of the pump, *R*, a current of air is drawn through each drum to the centre, whence it passes through the tube, *V*, to a cooling coil, *S*, to condense the small amount of acetic acid vapour it carries over.

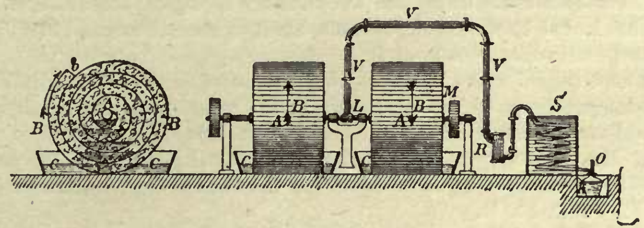

FIG. 248.

Another continuous and very rapid method, which avoids loss of acetic acid or aldehyde and diminishes the labour necessary by establishing more intimate contact between the alcoholic liquid and the subdividing material, is that in which the *stave acetifier* (Figs. 249 and 250) is used. This consists of a wooden box, *P*, about 1 metre wide and 2 metres high, terminating at the top in a channel, *R*. The box is filled with nine or ten layers of thin beech sticks, placed vertically and very close one to the other. The position of the sticks in one layer is crossed with respect to that of the sticks in the next layer. These sticks are held apart by small strips of wood so as to allow of the passage of a thin film of liquid downwards and of the air upwards. The total surface of the sticks in an apparatus of the dimensions stated above amounts to more than 1000 sq. metres, so that the oxidation is extraordinarily rapid, while the working, which may continue uninterruptedly for years, is extremely regular and simple. The air enters at a lateral slit, *Z*, at the bottom, this being covered with gauze to prevent access of harmful insects, and the draught is regulated by a slider in the exit-channel, *R*; the vinegar is discharged at *E*. The thermometer, *T*, shows the temperature of the air as it leaves. The figure shows also the contrivance for feeding the apparatus regularly and continuously with the alcoholic liquid. The latter is contained in the tank, *B*, in which is a wooden float, *F*, moving along three vertical rods, *L*, and carrying the glass siphon, *W*, terminating in a rubber tube with a regulating clip, *n*. The liquid from the siphon falls into a tube, *G*, and thence through the tube, *A C*, to the vessel, *H* (3 litres capacity), and, when this is full, it discharges through the siphon, *r*, on to the perforated plate, *V*, which distributes the liquid as a fine spray over

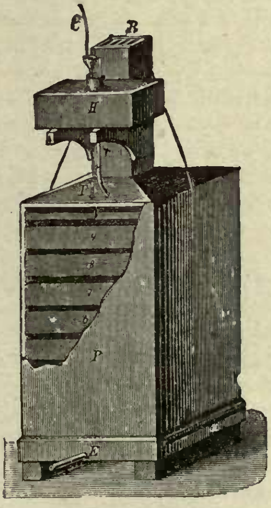

FIG. 249.

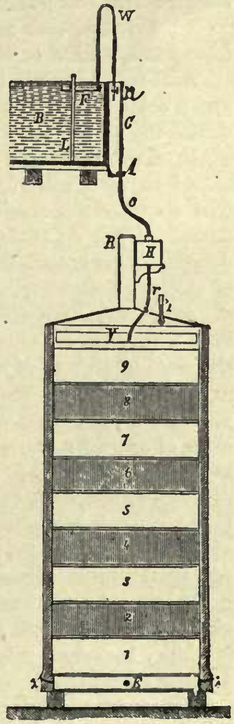

FIG. 250.

the bundles of sticks, and is traversed by several glass tubes to allow of the escape of the ascending air. In this way the flow of liquid from *B* is independent of the amount of liquid present in it at any instant (that is, of the pressure it exerts). The clip, *n*, is regulated so that the vessel, *H*, is refilled and discharges its 3 litres of liquid every one or two hours (or in any other prearranged time).

Attempts have been made to replace the ordinary biological acetification by chemical oxidation of the alcohol by means of platinum black or even of ozone, but neither method has attained to practical importance.

Vinegar is kept in *full* casks in stores like those used for wine, but it is not injured by a high air-temperature. An excess of air in the vessels and the continued presence of the mother-of-vinegar lower its strength, and, when this becomes too low, putrefaction may develop. Its keeping properties and aroma may be enhanced by pasteurisation (*see* pp. 186, 210) at 50° to 60°. A weak vinegar may be strengthened and kept if a little *pure* acetic acid is added to it.

WINE VINEGAR (white or red) is distinguished from other vinegars by its aroma, due partly to ethyl acetate and to small proportions of aldehydes. It usually contains 6 to 9 per cent. of acetic acid and less than 1 per cent. of alcohol, and has the density 1·015 to 1·020. The extract and the ash have the same compositions as those of wines, the former being rich in cream of tartar.

BEER VINEGAR contains 4·5 to 6 per cent. of extract rich in maltose, dextrin, albuminoids, and phosphates, and exempt from cream of tartar.

This vinegar also contains less acetic acid and, since it does not keep so well as that from wine, is used to break down excessively strong vinegars.

ARTIFICIAL VINEGARS, prepared from purely alcoholic liquids or from acetic acid and a colouring material such as caramel, have very little extract and no cream of tartar, whilst the percentage of acetic acid sometimes reaches 12 or 13.

In the **ANALYSIS OF VINEGAR**, the density of the extract and the ash are determined as with wine (p. 186). The content of acetic acid cannot be estimated exactly with standard alkali solution, since other acids (tartaric, succinic, etc.) present influence the titration; nor do the graduated tubes (*acetometers*) give accurate results. A more exact determination is effected by distilling the acetic acid in a current of steam, as in the analysis of calcium acetate (p. 337).

Adulteration of vinegar, which is somewhat frequent, is detected by the following tests: Real wine vinegar exhibits certain relations between the acetic acid and extract. In wine the ratio is 4 parts of alcohol for about 1 of extract, after deduction of the sugar present in sweet wines; assuming a loss of 15 per cent. of the alcohol during the conversion into vinegar, a pure wine vinegar with 5·31 per cent. of acetic acid should contain 1·08 per cent. of extract; one with 7·15 per cent. of acid, 1·44 per cent. of extract; one with 8·9 per cent. of acid, 1·8 per cent. of extract, and one with 10·7 per cent. of acid, 2·16 per cent. of extract, the ratio of acid to extract always being about 4·9 : 1. Addition of malt or beer vinegar is recognised by its reduction of Fehling's solution, or by concentrating 80 c.c. of the vinegar to about 2 c.c. and then adding alcohol: the formation of a white precipitate (dextrin) soluble in much water indicates such adulteration with certainty.

If mineral acids have been added, 4 or 5 drops of a dilute alcoholic solution of methyl violet (1 : 10,000) will give a greenish colour with 25 c.c. of the vinegar; also, with zinc sulphide, hydrogen sulphide is evolved; finally, after the vinegar has been heated with a trace of starch, it will not give a blue colour with iodine. The presence of sulphuric acid in vinegar is detected by the white precipitate formed with barium chloride, hydrochloric acid by that given by silver nitrate, and oxalic acid by the formation of a white precipitate with calcium chloride.

Artificial colouring-matters are detected in the same way as in wine and beer, and pyroligneous acid by the furfural reaction (*see this*).

The *price* of good wine vinegar is little less than that of wine, but artificial vinegars are cheaper.

France produces annually 600,000 to 700,000 hectolitres of vinegar, but in Italy the production is much less, owing to the competition of artificial vinegar and to the excessive duty of 17*s.* 6*d.* per hectolitre; in 1904–1905 the thirty-eight Italian vinegar factories consumed 6160 hectolitres of alcohol, the output of artificial vinegar being 60,000 hectolitres. In 1912 55,000 hectolitres of artificial vinegar were made. In Germany 70 per cent. of the vinegar is made from alcohol, the consumption of the latter being 41,110 hectolitres in 1911–1912 and 23,000 hectolitres in 1912–1913.

DERIVATIVES OF ACETIC ACID

SALTS OF ACETIC ACID. These are termed acetates, and are all soluble in water (the least soluble are silver and mercurous acetates). They are readily formed by neutralising acetic acid with metallic oxides or carbonates, previously dissolved in water. Pure anhydrous acetic acid or its alcoholic solution does not decompose alkaline carbonates, so that CO_2 precipitates potassium carbonate from an *alcoholic* solution of potassium acetate, acetic acid being liberated.

Even in aqueous solution, acetic acid undergoes only slight dissociation, but the acetates are considerably dissociated and diminish the dissociation and hence the acid characters of acetic acid (*see* Vol. I., p. 100).

POTASSIUM ACETATE (Normal), $CH_3 \cdot COOK$, melts at 229° and is soluble in water or alcohol. It is obtained by neutralising potassium hydrogen carbonate ($KHCO_3$) solution with acetic acid and evaporating to dryness. The *acid acetate*, $CH_3 \cdot COOK, C_2H_4O_2$, is obtained by dissolving the normal acetate in acetic acid and separates from the latter in crystals which melt at 148° and decompose at 200°, liberating anhydrous acetic acid.

A Diacid Potassium Acetate, $CH_3 \cdot COOK, 2C_2H_4O_2$, melting at 112°, is also known.

The commercial refined normal acetate costs about £3 per cwt.

SODIUM ACETATE, $CH_3 \cdot COONa$, crystallises from water with $3H_2O$, melts at 100°, loses water and solidifies at a higher temperature and then melts only at 319°.

In the cold it dissolves to some extent (1 : 23) in alcohol or in its own weight of water, giving a feebly alkaline solution and considerable lowering of temperature.

It is prepared by neutralising pyroligneous acid almost completely with sodium carbonate and concentrating the solution (after removal of the tar from the surface) to 27° Bé.; the crystals which separate on cooling are centrifuged, but are always reddish brown. The mother-liquors (which readily become mouldy) are taken to dryness and lightly roasted to burn the tarry products. Crude sodium acetate is preferably prepared by treating calcium acetate solution with sodium sulphate and then with a little soda to precipitate all the lime; the filtered or decanted solution is evaporated to dryness, heated to 250°, redissolved in water, concentrated, and allowed to crystallise.

According to C. Bauer, pure sodium acetate, free from the reddish-brown colour, may be prepared directly from pyroligneous acid by neutralising with sodium carbonate, and adding to the solution concentrated to 27° Bé., 2 per cent. of caustic soda, the liquid being then allowed to crystallise in wide and shallow wooden vessels. The crystals are separated by centrifugation and redissolved, the small amount of free caustic soda being then neutralised with commercially pure acetic acid; the solution is boiled to expel the excess of acetic acid, concentrated to 27° Bé., and left to crystallise.

Acid sodium acetates are also known.

Sodium acetate serves for the preparation of pure acetic acid, and is used in dyeing, etc.

Before the war, crude red sodium acetate was sold, according to its degree of purity, at 14*s.* to 18*s.* per cwt.; the white purified crystals (pharmaceutical) at 24*s.* to 28*s.*; and the doubly refined and fused anhydrous product at 52*s.*

AMMONIUM ACETATE, $CH_3 \cdot COONH_4$, is obtained by neutralising hot glacial acetic acid with a current of dry ammonia or with ammonium carbonate. The pure crystals which separate melt at 113° to 114° and, although not highly hygroscopic, dissolve readily in water, giving an alkaline solution; the solution in acetic acid deposits the acid acetate melting at 66°. The salt acts as a sudorific and dissolves lead oxalate and sulphate. It is used to some extent in dyeing.

The commercial brown solution at 10° Bé. costs £1 per cwt. and the pure solution of the same density 25*s.*; chemically pure crystals cost £5 per cwt.

CALCIUM ACETATE, $(CH_3 \cdot COO)_2Ca + 2H_2O$. The preparation of the commercial product has already been described on p. 336. The pure salt is obtained by repeated crystallisation from water, and costs up to 48*s.* per cwt. Its solubility in water diminishes with rise of temperature up to a certain point and subsequently increases. For Statistics, *see* p. 339.

FERROUS ACETATE (Pyrolignite of Iron), $(CH_3 \cdot COO)_2Fe$. The crude product, used as a mordant in the dyeing and printing of textiles, is obtained from pyroligneous acid and iron filings, or from calcium pyrolignite and a concentrated solution of ferrous acetate; the tarry substances present preserve it from oxidation. A solution of 20° Bé. costs 6*s.* per cwt. and one of 30° Bé. 8*s.* 6*d.* The pure product is prepared by dissolving freshly prepared ferrous hydroxide in 30 per cent. acetic acid.

FERRIC ACETATE, $(C_2H_3O_2)_3Fe$, used as a mordant in dyeing, is obtained from the ferrous salt and sodium acetate. It gives a reddish-brown solution in the cold, but in the hot and in presence of a large amount of water, a reddish-brown mass of basic ferric acetate, $Fe(C_2H_3O_2)_2OH$, separates; it is this which fixes the colouring-matters.

ALUMINIUM ACETATE (Normal), $Al(C_2H_3O_2)_3$, is obtained from aluminium sulphate and the corresponding quantity of lead acetate. It is known only in solution, in which it gradually undergoes spontaneous decomposition into acetic acid and the basic acetate: $Al(C_2H_3O_2)_3 + H_2O = Al(C_2H_3O_2)_2OH + C_2H_4O_2$.

When the solution of the basic acetate is boiled, aluminium hydroxide and acetic acid separate: $Al(C_2H_3O_2)_2OH + 2H_2O = Al(OH)_3 + 2C_2H_4O_2$.

It is used in dyeing, in the printing of textiles and in the preparation of *waterproof fabrics.* For the last purpose, the material is first soaked in aluminium acetate solution and then heated or steamed, $Al(OH)_3$ thus being deposited in the pores of the fabric, which is rendered impervious to water.

BASIC ALUMINIUM ACETATE, $Al(C_2H_3O_2)_2OH + 1\frac{1}{2}H_2O$, is obtained crystalline by evaporating a solution of the normal acetate cautiously at a temperature not exceeding 38°; it is soluble in water. Dilute solutions (4 to 5 per cent.) of the normal acetate gradually deposit, on the walls of the containing vessel, a porcelain-like crust of a basic acetate with $2H_2O$ or $2\frac{1}{2}H_2O$: this is insoluble in water.

It is used, like the normal salt, in dyeing, textile-printing, etc.

SILVER ACETATE, $C_2H_3O_2 \cdot Ag$, is obtained crystalline by adding silver nitrate to a concentrated solution of an acetate (*e. g.*, that of ammonium). It is a characteristic salt, crystallising from water in shining needles (solubility 1 : 100 at 20°, 2·5 : 100 at 80°). When calcined in a porcelain crucible, it leaves, like all organic silver salts, pure metallic silver.

NORMAL LEAD ACETATE (Sugar of Lead), $(CH_3COO)_2Pb + 3H_2O$, forms monoclinic plates or crystals, has a disagreeable, sweetish taste, is poisonous, and exhibits a faintly acid reaction. It is slightly soluble in alcohol and more so in water (1 part dissolves in 1·5 parts of water at 15°, in 1 part at 40°, or in 0·5 part at 100°). It loses the water of crystallisation over sulphuric acid or at 100° and then melts above 200°.

It is used as a mordant in the dyeing and printing of textiles and also in the preparation of various lead salts and paints and certain pharmaceutical products; further, for conferring hot-drying properties on linseed oil to be used for varnishes.

Italy produced 45 tons in 1904, 80 in 1906, 140 in 1908, 200 (£5280) in 1911, 39 in 1914, and 200 (£12200) in 1915. Germany exported 1765 tons in 1905, 2078 (£52,000) in 1906, 1677 in 1909, 1288 in 1910, 2080 in 1911, 1664 in 1912, and 1626 in 1913.

The refined crystalline product was sold before the war at 24*s.* to 28*s.* per cwt., and the chemically pure at 36*s.*

It is best prepared commercially by the Bauschlicher-Bauer method (1892–1905) from commercial pure 60 per cent. acetic acid (*see* Tests on pp. 338 and 340) and pure litharge containing 99 per cent. of PbO.[1] A pitch-pine vat is fitted with a tight cover with three apertures: the central one for the shaft of a wooden stirrer, another for a copper cooling coil to condense the acetic acid vapours, and the third for the neck of a large wooden hopper, by means of which the litharge is dropped on to a wooden distributing roller provided with teeth and placed under the lid. The required quantity of acetic acid is heated to 60° by a copper steam coil in the bottom of the vat, and the litharge

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[1] It should contain neither iron, which would colour the crystals, nor aluminium, which would render filtration difficult.

gradually added in the proportion of 103 kilos per 100 kilos of 60 per cent. acetic acid; each 100 kilos added requires about an hour to dissolve if the stirrer is kept in motion and the temperature does not exceed 65°. The solution has a density of 70° to 72° Bé. and, if it does not show an acid reaction, it is slightly acidified with acetic acid,[1] and the mother-liquor (35° to 37° Bé.) from a preceding operation added in such amount that the density becomes 50° to 52° Bé. The solution at 65° is then allowed to clarify in a couple of tightly closed wooden vats, each fitted with a horizontal rail carrying strips of lead dipping into the liquid so as to remove the small amount of copper present. After five to six hours the solution is passed through a cloth filter-press with wooden channels, and is then left to crystallise in wooden vessels for eight to ten days—until the density of the mother-liquor falls to 35° Bé. in winter or 37° in summer. If the solution is kept at 60°, as crystals separate the vessel may be fed with fresh, more concentrated solution until a thick layer of crystals is obtained; it is then allowed to cool for some days. After the liquid has been decanted, the mass of small crystals (more concentrated and hotter solutions give larger crystals) is treated in a copper centrifuge and dried in wooden boxes placed in a vacuum apparatus at a temperature not exceeding 30°.[2]

MONOBASIC LEAD ACETATE (Subacetate of Lead), $(C_2H_3O_2)_2Pb + PbO + H_2O$, and **Dibasic Lead Acetate**, $(C_2H_3O_2)_2Pb + 2PbO$, are obtained by melting the normal acetate with a greater or less proportion of litharge (3 : 1 for the monobasic salt) on the water-bath; the former is readily soluble and the latter only slightly so (1 : 18 at 20° and 1 : 5·5 at 100°) in water. The *lead acetate of the pharmacopœia* is a 2 per cent. solution of the monobasic salt, and is used as a medicine; this salt is used also for weighting silk, for decolorising vegetable juices, and for preparing white lead and aluminium acetate. The anhydrous salt formerly cost 52*s.* per cwt.

NORMAL CHROMIC ACETATE, $Cr(C_2H_3O_2)_3 + H_2O$, is obtained from calcium or lead acetate and chrome alum or chromic sulphate. It gives a violet solution, which becomes green, without decomposing, when heated.

Basic Chromium Sulphate is obtained in a similar way from basic chromium sulphate or by adding ammonia or sodium hydroxide or carbonate to a solution of the normal acetate. The basicity increases with the amount of alkali, the compound, $Cr_2(C_2H_3O_2)_5OH$, being gradually converted into $Cr_2(C_2H_3O_2)_2(OH)_4$ or even more basic salts still. The more basic the acetate the more will it decompose on boiling and the more readily it will serve as a mordant in dyeing or, better, in printing, since the reducing action of the textile fibres or of the colouring-matters or of other organic substances added, results in the separation of the true mordant, $Cr(OH)_3$, which forms stable lakes with the dyes (alizarin, hæmatein from log-wood, etc.).

Commercial chromium acetate solutions at 20° Bé. were sold before the war at 16*s.* per cwt., those of 40° Bé. at 28*s.*, and the solid at 60*s.*; the chemically pure acetate cost 8*s.* per kilo.

STANNOUS ACETATE, $Sn(C_2H_3O_2)_2$, is obtained by treating stannous chloride with lead acetate or by dissolving freshly precipitated stannous hydroxide in dilute acetic acid. Its solution is used as a mordant or corrosive in printing cotton with substantive dyes (*see this*, Part III).

The 20° to 22° Bé. solution formerly cost 24*s.* per cwt.

NORMAL CUPRIC ACETATE (Crystallised Verdigris), $Cu(C_2H_3O_2)_2 + H_2O$, is obtained by dissolving the basic acetate (true verdigris) in acetic acid or, better, by decomposing copper sulphate solution with lead acetate. It forms clinorhombic, dark green prisms and is readily soluble in hot water (1 : 5) or in alcohol. It is used in medicine and has been suggested as a means of combating the *Peronospora* which attacks the vine. Before the war it cost 2*s.* 6*d.* per kilo.

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[1] The subsequent crystallisation is rendered difficult if the solution contains basic acetate, the presence of this being inferred from the turbidity produced on mixing a little of the liquid with an equal volume of 1 per cent. corrosive sublimate solution.

[2] *Analysis of lead acetate* is effected by dissolving 5 grams of it in water, precipitating the lead with a known quantity, in slight excess, of normal sulphuric acid, making up to 250 c.c., and then adding a volume of water about equal to that of the precipitate. In 50 c.c. of the filtrate, the sulphuric acid is precipitated with barium chloride, the weight of the resulting barium sulphate giving the quantity of sulphuric acid which has remained in combination with the lead. Another 50 c.c. of the filtrate is titrated with normal caustic potash, the total acidity thus found being due to acetic acid and excess of sulphuric acid; deduction of the latter then gives the amount of acetic acid existing in combination in the lead acetate.

BASIC COPPER ACETATE (Verdigris), $[2Cu(C_2H_3O_2)OH] + 5H_2O$, is obtained by arranging sheets of copper with flannel saturated with hot vinegar, acetic acid, or acid vinasse, in between. The crust of acetate is detached from the plates and sold in cakes either dry or with 30 to 40 per cent. of moisture. It forms blue needles or scales, which effloresce in the air and become green, owing to loss of water.

It dissolves only slightly in water and, when heated in the dry state, gives off acetic acid and water. When pure, it is completely soluble in excess of ammonium carbonate solution.

It was formerly used as a colouring-matter, but is now used for the preparation of *Schweinfurth's green* (*copper aceto-arsenite*), $Cu(C_2H_3O_2)_2, 3CuAs_2O_4$, by mixing with the requisite proportion of arsenious anhydride solution; this gives a beautiful green colouring-matter, which is still used to some extent, although it is very poisonous owing to the evolution of hydrogen arsenide in the air.

In cakes or balls, the basic acetate formerly cost £3 per cwt., whilst the refined powder cost £4 to £5.

PROPIONIC ACID, $C_3H_6O_2$ or $CH_3 \cdot CH_2 \cdot COOH$

This acid is obtained by hydrolysing ethyl cyanide (*see* p. 238), or by oxidising propyl alcohol with chromic acid, or by the action of certain micro-organisms on calcium lactate. It is, however, usually prepared by fermenting wheat-bran, or is extracted from crude pyroligneous acid, being formed in small quantity (2 to 4 per cent.) in the dry distillation of wood. For some years it has been manufactured by the Effront process (*see* p. 183) from the residues of beetroot *molasses*: 1000 kilos of molasses yield 75 kilos of ammonium sulphate and 95 to 120 of fatty acids consisting largely of propionic acid (*see also* section on Sugar).

It occurs in perspiration, in the fruit of *Gingko biloba*, and in colophony tar.

It is a liquid of sp. gr. 0·996 at 19° and resembles acetic acid in odour and in physical and chemical properties. It is, indeed, not possible to separate these two acids by distillation and rectification, but this may be done by means of the lead salts, *basic lead propionate*, $3Pb(C_3H_5O_2)_2, 4PbO$, being very slightly soluble in hot water, although soluble in cold. It boils at 141° and solidifies at –22°. It forms crystalline salts soluble in water, and its esters have a fruity aroma. Chemically pure propionic acid formerly cost 32*s*. per kilo, and the commercial acid 14*s*. 6*d*., but nowadays the Effront process yields a much cheaper commercial acid, which in practice may be used to replace formic and acetic acids, these being more difficult to purify.

BUTYRIC ACIDS, $C_4H_8O_2$

Two isomerides are known of different structures, their constitutional formulæ being deduced from their methods of synthesis.

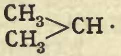
(1) **NORMAL BUTYRIC ACID** (Butanoic or Propylcarboxylic Acid or Butyric Acid of Fermentation), $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$, is the more important of the two isomerides and exists in butter in the form of glyceric ester to the extent of 4 to 5 per cent. It is formed also in sweat and occurs in solid excreta and in decomposing cheese, as well as among the products of fermentation of glycerine.

It is obtained practically, not by synthesis (*see* p. 320), but by the butyric fermentation of starch-paste in presence of a little tartaric acid, putrefied meat or cheese being added after a few days (pure cultures of special bacteria are also used at the present time); it is obtained also from acid skim milk by treatment with powdered marble and converting the calcium lactate into calcium butyrate, then into the sodium salt, and finally, by means of H_2SO_4, into the free acid. It is also obtained from molasses residues by Effront's process (*see above*).

It forms an oily liquid, sp. gr. 0·958 at 14°, boiling at 162° and solidifying in scales at 19°. It dissolves in water, alcohol, or ether, burns with a bluish flame, and gives crystalline, slightly soluble salts.

Calcium Butyrate, $(C_4H_7O_2)_2Ca + H_2O$, is less soluble in hot than in cold water.

The *esters* have pleasant, fruity odours, and are used to produce artificial rum. Commercial concentrated butyric acid cost before the war 4*s*. per kilo; the 50 per cent. acid, 2*s*. 6*d*.; and the chemically pure (100 per cent.), 5*s*. 10*d*. The concentrated esters were sold at 2*s*. 6*d*. to 5*s*. per kilo.

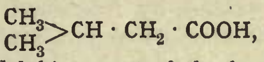
(2) **ISOBUTYRIC ACID** (2-Methylpropanoic or Dimethylacetic Acid),  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot COOH$, resembles the preceding acid, but is less soluble in water. It boils at 154° and solidifies at — 79°, and occurs free in arnica and carob roots and as ester in chamomile oil. It may be obtained by the ordinary synthetic processes and is less resistant than the normal acid to oxidising agents. The pure acid formerly cost 40*s*. per kilo and the commercial acid about one-half as much.

The Calcium Salt, $Ca(C_4H_7O_2)_2$, is more soluble in hot water than in cold.

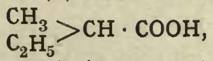
VALERIC ACIDS, $C_5H_{10}O_2$

The four isomerides predicted by theory are known.

(1) **NORMAL VALERIC ACID** (Pentanoic or Propylacetic Acid), $CH_3 . [CH_2]_3 . COOH$, is a dense liquid (sp. gr. 0·956 at 0°), boiling at 185° and solidifying at — 58·5°. It is obtained synthetically from propylmalonic acid or butyl cyanide, and is met with in pyroligneous acid; it is slightly soluble in water. The pure product cost before the war 5*d*. per gram.

(2) **ISOVALERIC ACID**,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2\cdot COOH$, is found free or in the form of esters in animals (fat of the dolphin, sweat of the feet, etc.) and vegetables (roots of *Valeriana officinalis*), and from the latter may be extracted by boiling with solutions of soda or by distilling with water containing phosphoric acid. It is a liquid (sp. gr. 0·947 at 0°), boiling at 174° and solidifying at –51°; it has a disagreeable odour of stale cheese. It is often obtained by oxidising fusel oil with dichromate and sulphuric acid. The pure acid costs 96*s*. per kilo.

Its esters are used as *artificial fruit essences*, and cost from 10*s*. to 16*s*. per kilo.

(3) **ETHYLMETHYLACETIC ACID** (Methyl-2-butanoic or Active Valeric Acid),  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH\cdot COOH$, is optically active, as it contains an asymmetric carbon atom (*see* p. 19); it occurs naturally with isovaleric acid. The inactive mixture of the two oppositely active acids may be resolved into its active components by means of the brucine salts. It boils at 174°.

(4) **TRIMETHYLACETIC ACID** (Dimethyl-2-propanoic or Pivalic Acid), $(CH_3)_3 \vdots C\cdot COOH$, is a solid, m.-pt. 35°, b.-pt. 163°. It has an odour resembling that of acetic acid, and it may be obtained from tertiary butyl cyanide.

HIGHER ACIDS

Of the numerous isomerides theoretically possible and of the many actually known, mention will be made only of some of the more important which occur naturally and are usually of the normal structure and with even numbers of carbon atoms.

NORMAL CAPROIC ACID, $C_6H_{12}O_2$ or $CH_3\cdot [CH_2]_4\cdot COOH$, is a liquid boiling at 205° and solidifying at –1·5°. It is volatile in steam, has an unpleasant odour like rancid butter, and is found free in Limburger cheese and coco-nut oil, and as glyceride in goats' butter. It is formed on oxidising proteins or higher fatty acids (unsaturated).

HEPTOIC ACID (Œnantic Acid), $C_7H_{14}O_2$ or $CH_3\cdot [CH_2]_5\cdot COOH$, is formed on oxidation of castor oil or *œnanthaldehyde*. It is a liquid boiling at 220° and solidifying at — 20°. It differs from its lower homologues by exhibiting a slight odour of fat.

CAPRYLIC ACID (Octoic Acid), $C_8H_{16}O_2$ or $CH_3\cdot [CH_2]_6\cdot COOH$, solidifies at 16·5° and boils at 237·5°; it is found in coco-nut oil and as glyceride in ordinary butter and that of goats.

NONOIC ACID (Pelargonic Acid), $C_9H_{18}O_2$ or $CH_3\cdot [CH_2]_7\cdot COOH$, is a liquid boiling at 254°. It is formed by oxidising oleic acid or by decomposing the *ozonide of oleic acid* (Molinari and Soncini, 1905) with dilute alkali. In nature it occurs in *Pelargonium roseum*.

DECOIC ACID (Capric Acid), $C_{10}H_{20}O_2$ or $CH_3 \cdot [CH_2]_8 \cdot COOH$, is a solid, melting at 31·4° and boiling at 200° under 100 mm. pressure. It also is found in coco-nut oil and goats' butter.

UNDECOIC ACID, $C_{11}H_{22}O_2$ or $CH_3 \cdot [CH_2]_9 \cdot COOH$. Distillation of castor oil under reduced pressure yields the unsaturated *undecenoic acid*, $C_{11}H_{20}O_2$, which gives undecoic acid on reduction with hydrogen. It melts at 28° and boils at 212° (100 mm.).

LAURIC ACID, $C_{12}H_{24}O_2$ or $CH_3 \cdot [CH_2]_{10} \cdot COOH$, is a solid, melting at 44° and boiling at 225° (100 mm.); it occurs in the form of glyceride in laurel berries.

MYRISTIC ACID, $C_{14}H_{28}O_2$ or $CH_3 \cdot [CH_2]_{12} \cdot COOH$, melts at 54° and boils at 248° (100 mm.). It is found as glyceride (*myristin*) in the nutmeg (*Myristica moschata*) and in ox-gall, and abounds in the seeds of *Virola Venezuelensis*.

PALMITIC ACID (Hexadecoic Acid), $C_{16}H_{32}O_2$ or $CH_3 \cdot [CH_2]_{14} \cdot COOH$, forms a moderately transparent white mass, which readily softens and melts at 62·6°. It is insoluble in water and crystallises from alcohol in scales or needles. It boils unchanged at 268° under 100 mm. pressure, or, with partial decomposition, at 339° to 356° under the ordinary pressure.

It is one of the normal components of animal and vegetable fats, in which it occurs as a glyceride (palmitin), and is easily obtained, together with oleic acid, from palm oil by hydrolysing and then decomposing the soap formed; the palmitic acid is then isolated by fractional crystallisation. *Japanese vegetable wax* or *Carnauba wax* consists almost exclusively of palmitin. The industrial treatment of fats and oils for the extraction of the corresponding fatty acids (palmitic, stearic, and oleic) will be described in the section dealing with the manufacture of soap and candles.

Commercial palmitic acid is also known by the inaccurate name of *palmitin* and is likewise manufactured by melting oleic acid with potassium hydroxide (*Varrentrapp's reaction*): $C_{18}H_{34}O_2 + 2KOH = H_2 + CH_3 \cdot CO_2K + C_{16}H_{31}O_2K$ (potassium palmitate, which gives palmitic acid under the action of mineral acid).

Its alkali salts (*soaps*) are soluble in alcohol or water, but considerable dilution of the aqueous solutions results in the separation of an acid salt and liberation of alkali. Whilst in alcoholic solution these soaps show virtually normal molecular weights, the aqueous solutions show no rise in the boiling-point, the soaps thus behaving as colloids in these solutions (*see* Vol. I., p. 105). The other salts (*palmitates*) are insoluble in water and, in some cases, soluble in alcohol; mineral acids liberate palmitic acid from them.

Before the war, the commercial acid cost £2 per cwt., the refined product £4, and the doubly refined 25*s*. 6*d*. per kilo.

MARGARIC ACID, $C_{17}H_{34}O_2$ or $CH_3 \cdot [CH_2]_{15} \cdot COOH$, was for a long time thought to exist in fats, but it has been shown that a mixture of palmitic (C_{16}) and stearic (C_{18}) acids was being dealt with. Synthetically it is obtained by hydrolysing cetyl cyanide, $C_{16}H_{33} \cdot CN$, and by other methods. It melts at 60° and distils unchanged at 277° under 100 mm. pressure.

STEARIC ACID, $C_{18}H_{36}O_2$ or $CH_3 . [CH_2]_{16} . COOH$, which is improperly known commercially as *stearine* (and is then mixed with palmitic acid), and its separation from oleic acid, will be described when dealing with candles.

As glyceride, it occurs with that of oleic acid as one of the principal constituents of fats and oils, and is usually prepared industrially from beef suet.

Synthetically it may be obtained by the reducing action of hydrogen on oleic acid (*see this*), and the constitution of the latter being known, that of stearic acid follows directly. Industrial application is now made of this process (*see* Oleic acid).

It forms a somewhat soft white mass, melting at 69·3°, and crystallises from alcohol in shining scales. It boils unchanged at 287° under 100 mm.

pressure or with partial decomposition at 359° to 383° under the ordinary pressure.

It is insoluble in water, soluble slightly in light petroleum, and more readily in alcohol, ether, benzene, or carbon disulphide.

Its salts behave like those of palmitic acid. The lead salts of these high fatty acids are obtained by boiling the fats or oils with lead oxide and water. This *lead soap* is used for the preparation of *lead plaster*, which is used in medicine and in the manufacture of varnish. Stearic acid made into a paste with gypsum forms a kind of *artificial ivory.*

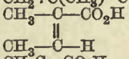
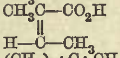
Italy imported, especially from France, England, and Belgium, the following amounts of stearic acid :

	1908	1910	1912	1913	1914	1915	1916	1917	1918
Tons .	1,250	1,445	621	920	698	423	119	58	152
Value, £	—	63,560	—	32,020	—	—	—	—	19,773

CEROTIC or **CEROTINIC ACID**, $C_{27}H_{54}O_2$, is found free in beeswax (together with Melissic Acid, $C_{30}H_{60}O_2$), as ester in Chinese wax and as glyceride in the fat of raw wool. It melts at 78·5° and is converted by oxidising agents into various acids with lower molecular weights.

II. UNSATURATED MONOBASIC FATTY ACIDS

A. OLEIC or ACRYLIC SERIES, $C_nH_{2n-2}O_2$ (Olefine-carboxylic Acids)

Empirical formula	Name of acid		Constitutional formula	Melting-point	Boiling-point
$C_3H_4O_2$	Acrylic acid		$CH_2:CH\cdot CO_2H$	13°	140°
$C_4H_6O_2$	Crotonic	Vinylacetic acid	$CH_2:CH\cdot CH_2\cdot CO_2H$	−39°	163°
		Solid crotonic acid	$CH_3\cdot CH:CH\cdot CO_2H$ (*cis*)	72°	181°
		Liquid crotonic acid	$CH_3\cdot CH:CH\cdot CO_2H$ (*trans*)	15·5°	169°
		Metacrylic acid	$CH_2:C(CH_3)\cdot CO_2H$	16°	161°
$C_5H_8O_2$	(8 structural isomerides and one stereoisomeride)	Angelic acid .	 $CH_3—C—CO_2H$ $\|\|$ $CH_3—C—H$	45°	185°
		Tiglic acid .	 $CH_3C—CO_2H$ $\|\|$ $H—C—CH_3$	65°	198·5°
$C_6H_{10}O_2$	(Not all stereoisomerides known)	Pyroterebic acid .	$(CH_3)_2:C:CH\cdot CH_2\cdot CO_2H$	−15°	207°
$C_7H_{12}O_2$	Do.	γ-Allylbutyric acid	$CH_2:CH\cdot[CH_2]_4\cdot CO_2H$	—	226°
$C_7H_{12}O_2$	Do.	Teracrylic acid .	$(CH_3)_2:C:C(CH_3)\cdot CH_2\cdot CO_2H$	—	218°
$C_{10}H_{18}O_2$	Do.	Citronellic acid .	$CH_2:C(CH_3)\cdot[CH_2]_3\cdot CH(CH_3)\cdot CH_2\cdot CO_2H$	—	152° (18 mm.)
$C_{11}H_{20}O_2$	Do.	Undecenoic acid .	$CH_2:CH\cdot[CH_2]_8\cdot CO_2H$	24·5°	213·5° (100 mm.)
$C_{16}H_{30}O_2$	Do.	Hypogæic acid .	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_5\cdot CO_2H$	—	—
$C_{18}H_{34}O_2$	Do.	Oleic acid . .	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$ (*cis*)	14°	223° (10 mm.)
		Elaidic acid .	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$ (*trans*)	51°	225° (10 mm.)
$C_{18}H_{34}O_2$	Do.	Iso-oleic acid .	$CH_3\cdot[CH_2]_8\cdot CH:CH\cdot[CH_2]_6\cdot CO_2H$ (?)	44°	—
		Δαβ-oleic acid .	$CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot CO_2H$	58°	—
$C_{22}H_{42}O_2$	Do.	Erucic acid .	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{11}\cdot CO_2H$	34°	254·5° (10 mm.)
		Brassidic acid .	$CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_{11}\cdot CO_2H$	65°	256° (10 mm.)
		Isoerucic acid .	$CH_3\cdot[CH_2]_8\cdot CH:CH\cdot[CH_2]_{10}\cdot CO_2H$ (?)	55°	—

The importance of these acids is due to the fact that certain of them occur as glycerides in many fats and oils.

GENERAL PROCESSES OF FORMATION. The following are the most important of these :

(1) The unsaturated halogen derivatives of unsaturated alcohols may be transformed into cyanogen derivatives, which give the corresponding acids on hydrolysis (*see* p. 238) :

$$CH_2:CH\cdot CH_2\cdot OH \rightarrow CH_2:CH\cdot CH_2\cdot Br \rightarrow$$
$$CH_2:CH\cdot CH_2\cdot CN \rightarrow CH_2:CH\cdot CH_2\cdot COOH.$$

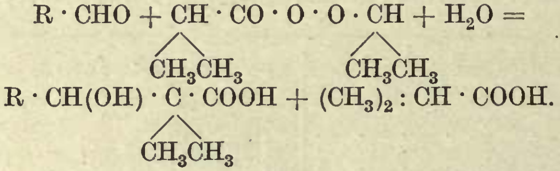
(2) Oxidation of unsaturated alcohols and aldehydes with mild oxidising agents (silver oxide or the oxygen of the air) which do not attack the double linking; allyl alcohol and acroleïn give acrylic acid.

(3) Of general use is *Perkin's reaction*, applicable especially to the aromatic series, but of service also for the fatty series: when an aldehyde is heated with the sodium salt of a saturated fatty acid in presence of an anhydride (*e. g.*, acetic anhydride) and then treated with water, the resulting products are the saturated acid corresponding with the aldehyde used and an unsaturated acid, which always has the double linking between the α- and β-carbon atoms, the α-carbon atom being that adjacent to the carbonyl group, CO. If the chain united to the aldehyde group is denoted by R, the intermediate phases of this reaction are probably as follow:

(*a*) $R\cdot CHO + CH_3\cdot CO\cdot O\cdot CO\cdot CH_3$ give, by aldol condensation, $R\cdot CH(OH)\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CH_3$; this unstable compound immediately separates water, giving $R\cdot CH : CH\cdot CO\cdot O\cdot CO\cdot CH_3$, treatment of this product with water yielding the unsaturated acid:

(*b*) $R\cdot CH : CH\cdot CO\cdot O\cdot CO\cdot CH_3 + H_2O = CH_3\cdot COOH + R\cdot CH : CH\cdot COOH.$

It is evident that, if only one hydrogen atom is united to the carbon atom adjacent to the carbonyl group of the original anhydride, the first phase of the reaction, but not the second, will be possible, so that only a saturated hydroxy-acid will be obtained:



$$R\cdot CHO + \underset{CH_3CH_3}{CH}\cdot CO\cdot O\cdot O\cdot \underset{CH_3CH_3}{CH} + H_2O =$$
$$R\cdot CH(OH)\cdot \underset{CH_3CH_3}{C}\cdot COOH + (CH_3)_2 : CH\cdot COOH.$$

The presence of the sodium salt of the fatty acid is indispensable to all these reactions, but its function has not yet been explained.

(4) Similar to *Perkin's synthesis* is the reaction between an aldehyde (or an α-ketonic acid, $R\cdot CO\cdot COOH$, which possibly loses CO_2 and thus gives an aldehyde) and malonic acid in presence of glacial acetic acid, a mixture of unsaturated monobasic acids with the double linking in the $\alpha\beta$- or $\beta\gamma$-position being obtained and CO_2 split off:

$$(a)\quad R\cdot CH_2\cdot CHO + \underset{\text{Malonic acid}}{CH_2<\begin{matrix}COOH\\COOH\end{matrix}} = R\cdot CH_2\cdot CH(OH)\cdot CH<\begin{matrix}COOH\\COOH\end{matrix}$$

$$(b)\quad 2R\cdot CH_2\cdot CH(OH)\cdot CH<\begin{matrix}COOH\\COOH\end{matrix} =$$
$$2CO_2 + 2H_2O + \underset{\alpha\,\beta\text{-acid}}{R\cdot CH_2\cdot CH : CH\cdot COOH} + \underset{\beta\,\gamma\text{-acid}}{R\cdot CH : CH\cdot CH_2\cdot COOH}.$$

It should be noted that this reaction always gives also a condensation product of 1 mol. of the aldehyde and 2 mols. of malonic acid, this product then losing CO_2 and yielding a saturated dibasic acid:

$$R\cdot CH<\begin{matrix}CH(COOH)_2\\CH(COOH)_2\end{matrix} = 2CO_2 + R\cdot CH<\begin{matrix}CH_2\cdot COOH\\CH_2\cdot COOH\end{matrix}$$

(5) When monohalogenated saturated fatty acids (especially those with the halogen in the β-position) are heated with alcoholic potash, or sometimes even with water alone, a molecule of halogen hydracid is eliminated and the unsaturated acid formed (similar to the reaction giving unsaturated hydrocarbons, p. 108):

$$\underset{\beta\text{-Iodopropionic acid}}{CH_2I\cdot CH_2\cdot COOH} = HI + \underset{\text{Acrylic acid}}{CH_2 : CH\cdot COOH}.$$

(6) By separating a molecule of water from monohydroxy-acids by means of distillation or a dehydrating agent (H_2SO_4, PCl_5, P_2O_5) or sometimes by merely heating with caustic soda solution, the unsaturated monobasic fatty acids are formed :

$$\underset{\beta\text{-Hydroxybutyric acid}}{CH_3 \cdot CH(OH) \cdot CH_2 \cdot COOH} = H_2O + \underset{\text{Crotonic acid}}{CH_3 \cdot CH : CH \cdot COOH.}$$

GENERAL PROPERTIES. The number of double bonds is ascertained by the same methods as are applied to unsaturated hydrocarbons (*see* p. 107)—by addition of either halogen or ozone. These unsaturated acids are more energetic than the corresponding saturated acids with the same numbers of carbon atoms, as may be seen from their ionisation constants (Vol. I., pp. 102 *et seq.*). They are more easily oxidisable than the corresponding saturated acids, powerful oxidising agents rupturing the carbon atom chain at the double linking, the position of which may hence be established by a study of the compositions of the two acids formed.

When boiled with 10 per cent. caustic soda solution, unsaturated acids with a double linking (Δ) in the $\beta\gamma$-position undergo displacement of this linking with the *partial* formation of unsaturated acids with a double bond in the $\alpha\beta$-position (Fittig, 1891–1894); this is formed from an intermediate hydroxy-acid, an equilibrium being established as indicated below :

$$\underset{\beta\,\gamma\text{-acid}}{R \cdot CH : CH \cdot CH_2 \cdot COOH} + H_2O \rightleftarrows \underset{\beta\text{-Hydroxy-acid}}{R \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot COOH} \leftrightarrows$$

$$H_2O + \underset{\alpha\,\beta\text{-acid}}{R \cdot CH_2 \cdot CH : CH \cdot COOH.}$$

In general this reaction preponderates towards the formation of the $\alpha\beta$-acid and not *vice versa,* the carboxyl group apparently exerting an attraction on the double linking.

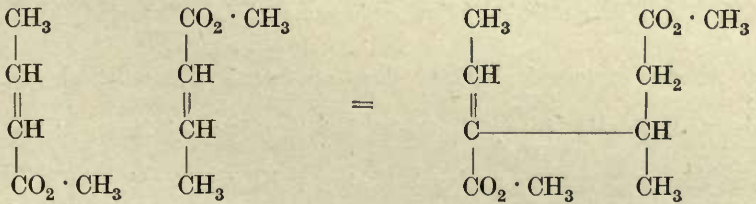
When an unsaturated acid is fused with caustic soda or potash, the double linking is displaced, giving an $\alpha\beta$-acid, the new molecule immediately splitting at the double bond, the resultant products being acetic acid and another saturated acid. This displacement of the double linking was unknown until a few years ago, so that oleic acid, for example, which gives palmitic and acetic acids quantitatively when fused with potash, was regarded as an $\alpha\beta$-unsaturated acid. It has, however, been shown (*see later*) that the double bond of oleic acid is in the middle of the molecule, the action of the potash causing displacement of this bond before the molecule is resolved :

$$\underset{\text{Oleic acid}}{CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_7 \cdot COOH} \rightarrow \underset{\alpha\,\beta\text{-Oleic acid}}{CH_3 \cdot [CH_2]_{14} \cdot CH : CH \cdot COOH}$$

$$CH_3 \cdot [CH_2]_{14} \cdot CH : CH \cdot COOH + 2KOH + O =$$

$$\underset{\text{Potassium palmitate}}{CH_3 \cdot [CH_2]_{14} \cdot COOK} + H_2O + CH_3 \cdot COOK.$$

The acids of the oleic or acrylic series, and unsaturated compounds in general, exhibit a tendency to *polymerise ;* the mere action of sodium alkoxide on the crotonic esters produces, in addition to other reactions, the following change :



Methyl crotonate Methyl dicrotonate

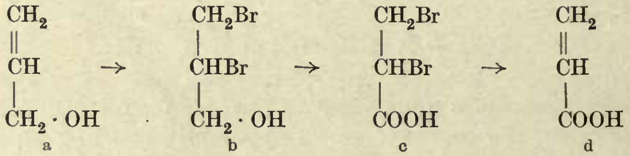
Instances of *stereoisomerism* among unsaturated compounds have already been described on pp. 21 and 22, and it is only necessary to state here that, of the two stereoisomerides corresponding with one and the same formula, one is less stable than the other, into which it is easily and directly transformed (the inverse change only takes place indirectly) by mere heating or by the action of concentrated sulphuric acid, caustic soda, a little nitrous acid, or a trace of bromine in the presence of light.

ACRYLIC ACID (Propenoic Acid)

$C_3H_4O_2$ or $CH_2 : CH \cdot COOH$

This acid was prepared for the first time (Redtenbacher, 1843) by oxidising acroleïn, $CH_2 : CH \cdot CHO$, with silver oxide. It is now more readily obtained indirectly, by the action of gaseous hydrogen chloride, which gives β-chloropropaldehyde, $CH_2Cl \cdot CH_2 \cdot CHO$, this being converted by nitric acid into the corresponding β-chloropropionic acid, $CH_2Cl \cdot CH_2 \cdot COOH$; when the last compound is boiled with a solution of alkali, it loses HCl, yielding acrylic acid.

Another convenient synthesis is the following: allyl alcohol (a, *see below*) with bromine gives dibromopropyl alcohol (b), which, on oxidation, yields αβ-dibromopropionic acid (c), and this, by the action of either zinc in presence of dilute sulphuric acid (or water) or reduced copper (containing iron) loses bromine and gives acrylic acid (d):



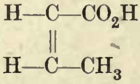
$$\underset{a}{\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2 \cdot OH\end{array}} \rightarrow \underset{b}{\begin{array}{c}CH_2Br\\ |\\ CHBr\\ |\\ CH_2 \cdot OH\end{array}} \rightarrow \underset{c}{\begin{array}{c}CH_2Br\\ |\\ CHBr\\ |\\ COOH\end{array}} \rightarrow \underset{d}{\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ COOH\end{array}}$$

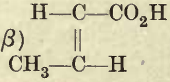
Acrylic acid is a liquid soluble in water and having a pungent odour almost like that of acetic acid: it has the sp. gr. 1·0621 at 16°, boils and polymerises at about 140°, and when cooled forms tabular crystals melting at 13°. With nascent hydrogen, it is transformed into propionic acid, whilst, when fused with potash, it gives acetic and formic acids.

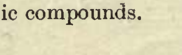
CROTONIC ACIDS, $C_4H_6O_2$

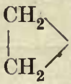
Isomeric unsaturated acids of this formula are possible theoretically—two stereoisomerides and the others structural isomerides. The following acids have actually been prepared:

(*a*) $CH_2 : CH \cdot CH_2 \cdot COOH$, *vinylacetic acid ;*

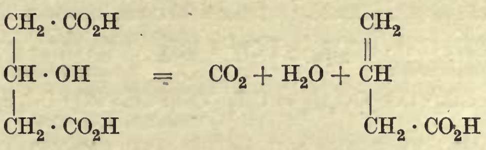
(*bα*)  $\begin{array}{l}H\text{—}C\text{—}CO_2H\\ \quad\ \|\\ H\text{—}C\text{—}CH_3\end{array}$, *cis* β-methylacrylic acid (*solid crotonic acid*);

(*bβ*)  $\begin{array}{l}\quad\ H\text{—}C\text{—}CO_2H\\ \qquad\ \ \|\\ CH_3\text{—}C\text{—}H\end{array}$, *trans* β-methylacrylic acid (*liquid crotonic acid*);

(*c*)  $CH_2 : C{<}^{CH_3}_{COOH}$, methylmethyleneacetic or α-methylacrylic acid.

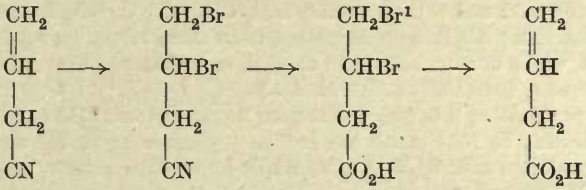
With the general formula, $C_4H_6O_2$, there corresponds also ethyleneacetic or trimethylenecarboxylic acid,  CH · COOH, but this does not belong to the olefinecarboxylic acids as it contains no double linking, and it will therefore be studied with the cylic compounds.

(*a*) **VINYLACETIC ACID,** $CH_2 : CH \cdot CH_2 \cdot CO_2H$, has been prepared, only recently, by distilling β-hydroxyglutaric acid in a vacuum:



$$\begin{array}{l} CH_2 \cdot CO_2H \\ | \\ CH \cdot OH \\ | \\ CH_2 \cdot CO_2H \end{array} = CO_2 + H_2O + \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 \cdot CO_2H \end{array}$$

and also by first brominating (with bromine dissolved in CS_2) allyl cyanide, hydrolysing the product, and finally removing the bromine by means of zinc dust and alcohol, thus:

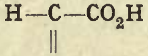


$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CN \end{array} \longrightarrow \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2 \\ | \\ CN \end{array} \longrightarrow \begin{array}{l} CH_2Br^1 \\ | \\ CHBr \\ | \\ CH_2 \\ | \\ CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

Vinylacetic acid is a very hygroscopic liquid, which solidifies when cooled to a low temperature; it melts at − 39° and boils at 163°. Its calcium salt, $(C_4H_5O_2)_2Ca, H_2O$, crystallises from water in shining needles.

When boiled with 5 per cent. sulphuric acid solution, it is transformed into the solid crotonic acid, $CH_2 : CH \cdot CH_2 \cdot COOH \rightarrow CH_3 \cdot CH : CH \cdot COOH$.

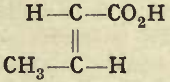
This transposition of the double linking is effected also by boiling with caustic soda solution, but in this case a preponderance of β-hydroxybutyric acid is formed at the same time.

(*ba*) **ORDINARY** or **SOLID CROTONIC ACID,**  $\begin{array}{l} H{-}C{-}CO_2H \\ \quad \| \\ H{-}C{-}CH_3 \end{array}$ (cis *β-methylacrylic acid* or cis *ethylideneacetic acid;* also wrongly known as *α-crotonic acid*). Its constitution follows from its synthesis from α-bromobutyric acid (or rather its ester) by the elimination of HBr under the action of alcoholic potash:

$$CH_3 \cdot CH_2 \cdot CHBr \cdot CO_2H = HBr + CH_3 \cdot CH : CH \cdot CO_2H.$$

From water (solubility 1 in 12) the acid crystallises in shining needles melting at 71° to 72°; it boils at 181° to 182°, has an odour resembling that of butyric acid, and is found free in crude pyroligneous acid. Its calcium and barium salts contain no water of crystallisation and are very soluble in water.

When gently oxidised in alkaline solution with permanganate, it gives *αβ-dihydroxybutyric acid,* $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$, which cannot form a *lactone,* so that neither of its hydroxyl groups is in the γ-position; the double linking of the crotonic acid must hence be between the α- and β-carbon atoms. When halogen hydracids are added to it, the halogen goes to the β-position. With nascent hydrogen it gives butyric acid.

(*bβ*) **LIQUID CROTONIC ACID,**  $\begin{array}{r} H{-}C{-}CO_2H \\ \| \quad\quad \\ CH_3{-}C{-}H \end{array}$ (trans *β-methylacrylic acid* or *isocrotonic* or *allocrotonic acid;* known improperly as β-crotonic acid). This acid is prepared from ethyl acetoacetate, which, with PCl_5, gives probably a chloracetic ester, the latter losing a molecule of HCl and yielding the two stereoisomeric chloroisocrotonic acids (or

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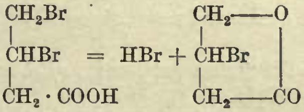
[1] This β γ-*dibromobutyric acid,* when boiled with water, gives a *β-bromobutyrolactone:*



$$\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2 \cdot COOH \end{array} = HBr + \begin{array}{l|} CH_2\text{——}O \\ | \\ CHBr \\ | \\ CH_2\text{——}CO \end{array}$$

Lactones are not usually formed by acids brominated in the α- or β-position, but only with those where the bromine atom is in the γ-position. It may hence be concluded that the double linking in vinylacetic acid is also in the β γ-position, since its brominated derivative gives a lactone, which is formed only when there is halogen in the γ-position.

the corresponding ethyl esters); these two isomerides may be separated, the one formed in greater proportion being readily, and the other difficultly, distilled in steam. The latter gives solid, and the other liquid, crotonic acid on reduction with sodium amalgam:

(a) $\underset{\text{Ethyl acetoacetate}}{CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OC_2H_5} + PCl_5 = \underset{\text{Intermediate product}}{CH_3 \cdot CCl_2 \cdot CH_2 \cdot CO \cdot OC_2H_5} + POCl_3.$

(b) $CH_3 \cdot CCl_2 \cdot CH_2 \cdot CO \cdot OC_2H_5 = \underset{\text{Two stereoisomerides}}{CH_3 \cdot CCl : CH \cdot CO \cdot OC_2H_5} + HCl.$

(c) $CH_3 \cdot CCl : CH \cdot CO \cdot OC_2H_5 + H_2 = \underset{\text{Ethyl ester of crotonic acid}}{CH_3 \cdot CH : CH \cdot CO \cdot OC_2H_5} + HCl.$

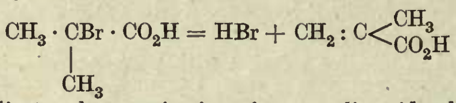
The isocrotonic acid thus obtained is liquid, but is not pure, as it always contains ordinary crotonic acid and a little *tetrolic acid*, $CH_3 \cdot C \vdots C \cdot CO_2H$. Only within recent years (1895 and 1904) has it been separated from these admixtures, either by means of its sodium salt, which is more soluble in alcohol, or by means of its quinine salt, which is less soluble in water, than that of crotonic acid.

After such purification it is found that pure liquid crotonic acid forms crystals melting at 15·5° and boiling at 169° under the ordinary pressure or at 74° under a pressure of 15 mm. The calcium salt, $(C_4H_5O_2)_2Ca, 3H_2O$, forms large prisms, and the barium salt, $(C_4H_5O_2)_2Ba, H_2O$, large plates.

When heated above 100°, it is converted partially into normal crotonic acid, and in order to avoid this change during distillation the operation is carried out in a vacuum; the transformation is instantaneous and quantitative in presence of a trace of bromine in aqueous solution or of carbon disulphide under the influence of direct sunlight.

That the structure of isocrotonic acid is the same as that of crotonic acid and not of vinylacetic acid is supported by the fact that isocrotonic acid gives no lactonic derivative (*see above*) and also by the fact that the *peroxyozonides* of these two acids, obtained by Harries and Langheld (1905) by the action of ozonised oxygen and having the structure $\begin{array}{l} CH_3 \cdot CH—CH \cdot C\begin{smallmatrix} \diagup OH \\ \diagdown O : O \end{smallmatrix} \\ \quad\;\;\, | \qquad\;\; | \\ \quad\;\; O \cdot O \cdot O \end{array}$, give with water the same decomposition products, namely, hydrogen peroxide, acetaldehyde, and glyoxylic acid, $CHO \cdot CO_2H$.

(c) **METHYLMETHYLENEACETIC ACID** (α-Methylacrylic, Metacrylic or Methylpropenoic Acid), $CH_2 : C{<}\begin{smallmatrix} CH_3 \\ CO_2H \end{smallmatrix}$, may be obtained by separation of water from α-hydroxyisobutyric acid and also by elimination of a molecule of HBr from α-bromoisobutyric acid:



$$\begin{array}{l} CH_3 \cdot CBr \cdot CO_2H = HBr + CH_2 : C{<}\begin{smallmatrix} CH_3 \\ CO_2H \end{smallmatrix} \\ \qquad\quad | \\ \qquad\; CH_3 \end{array}$$

This synthesis indicates the constitution of metacrylic acid, which is confirmed by the observation that reduction of this acid by means of sodium amalgam gives isobutyric acid, this having a known constitution.

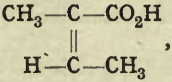
Metacrylic acid crystallises readily from water in shining prisms which melt at + 16° and boil at 161°, or at 60° to 63° under 12 mm. pressure. It has a strong but not unpleasant odour of bad mushrooms and occurs in Roman chamomile; it dissolves very readily in alcohol or ether. It exhibits a marked tendency to polymerise, more especially at 130°, but also in the cold when in contact with concentrated hydrochloric acid. The calcium salt forms crystals very soluble in water.

PENTENOIC ACIDS, $C_5H_8O_2$

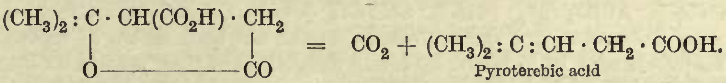
Several isomeric pentenoic acids are known, those which have been most closely studied being:

(a) **ANGELIC ACID** (α-Ethylidenepropionic, αβ-Dimethylacrylic or 2-Methyl-2-butenoic-1 Acid), $\begin{array}{l} CH_3—C—CO_2H \\ \qquad\;\; \| \\ CH_3—C—H \end{array}$. The double linking in this acid must be in the α β-position, and not in the γ-position, since lactonic derivatives are unknown. On protracted heating it is transformed into the stereoisomeric *tiglic acid.*

Angelic acid was first found in, and is still obtained from, the roots of *Angelica arcangelica*, and occurs as ester in Roman chamomile oil. The pure crystals melt at 45°, boil at 185°, and are only slightly soluble in water or volatile in steam.

(*b*) **TIGLIC ACID,**  $\begin{matrix} CH_3-C-CO_2H \\ \| \\ H-C-CH_3 \end{matrix}$, often occurs with angelic acid and is formed in the decomposition of various more complex organic compounds. It can be prepared synthetically from acetaldehyde and ethyl α-bromopropionate in presence of zinc, a hydroxy-acid being formed as an intermediate compound. It forms transparent crystals, m.-pt. 65°, b.-pt. 198·5°, and is slightly soluble in cold and readily in hot water; it has a pleasant smell and is volatile in steam.

PYROTEREBIC ACID (2-Methyl-2-pentenoic-5 Acid), $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C:CH\cdot CH_2\cdot COOH$, is formed by the distillation of an oxidation product (*terebic acid*) of oil of turpentine (together with the lactone of isocaproic acid, *see below*).

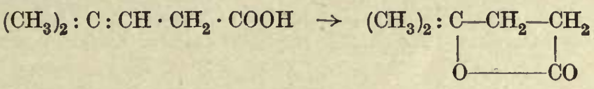


$$\begin{matrix} (CH_3)_2:C\cdot CH(CO_2H)\cdot CH_2 \\ | \qquad\qquad\qquad | \\ O\text{———————}CO \end{matrix} = CO_2 + (CH_3)_2:C:CH\cdot CH_2\cdot COOH.$$

Terebic ($\gamma\gamma$-dimethylparaconic) acid

Pyroterebic acid

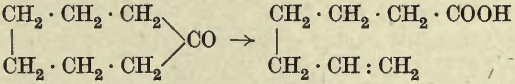
That pyroterebic acid really has this constitution is shown by the fact that, on reduction with hydriodic acid, it gives isocaproic acid of the known constitution $(CH_3)_2:CH\cdot CH_2\cdot CH_2\cdot COOH$. The position of the double linking is confirmed by the great ease with which it is converted into *isocaproic lactone* on prolonged boiling or by the action of a small quantity of hydrobromic acid:



$$(CH_3)_2:C:CH\cdot CH_2\cdot COOH \rightarrow \begin{matrix} (CH_3)_2:C-CH_2-CH_2 \\ | \qquad\quad | \\ O\text{————}CO \end{matrix}$$

Pyroterebic acid is a colourless liquid solidifying at − 15° and boiling at 207°; it is lighter than water, which dissolves it with difficulty.

γ-ALLYLBUTYRIC ACID (1-Heptenoic-7 Acid), $CH_2:CH\cdot[CH_2]_4\cdot CO_2H$, is obtained from *cycloheptanone* (or *suberone*) by *Wallach's reaction*, passing through the oxime, amine, etc.:



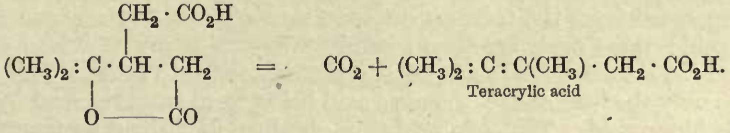
$$\begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}{>}CO \rightarrow \begin{matrix} CH_2\cdot CH_2\cdot CH_2\cdot COOH \\ | \\ CH_2\cdot CH:CH_2 \end{matrix}$$

Cycloheptanone

γ-Allylbutyric acid

It is a liquid boiling at 226° and, on oxidation, is converted into *adipic acid*, $COOH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$.

TERACRYLIC ACID (2 : 3-Dimethyl-2-pentenoic-5 Acid), $(CH_3)_2:C:C(CH_3)\cdot CH_2.COOH$, is homologous with pyroterebic acid and is also obtained by distilling an oxidation product (*terpenylic acid*) of oil of turpentine:



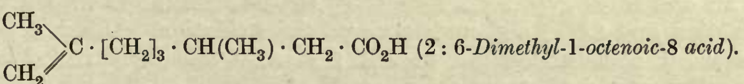
$$\begin{matrix} \qquad CH_2\cdot CO_2H \\ \qquad | \\ (CH_3)_2:C\cdot CH\cdot CH_2 \\ | \qquad\quad | \\ O\text{———}CO \end{matrix} = CO_2 + (CH_3)_2:C:C(CH_3)\cdot CH_2\cdot CO_2H.$$

Terpenylic acid

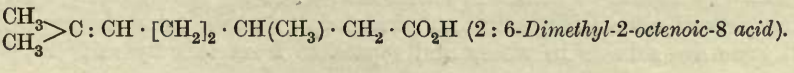
Teracrylic acid

It is a liquid, b.-pt. 218°, and is slightly soluble in water; with HBr it forms *heptalactone*, the γ-position of the double linking being thus confirmed.

CITRONELLIC ACID (Dextro-rotatory), $C_{10}H_{18}O_2$. It has not yet been definitely decided which of the two following formulæ must be attributed to this acid:



$$\genfrac{}{}{0pt}{}{CH_3}{CH_2}{>}C\cdot[CH_2]_3\cdot CH(CH_3)\cdot CH_2\cdot CO_2H \text{ (2 : 6-\textit{Dimethyl}-1-\textit{octenoic}-8 \textit{acid}).}$$



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C:CH\cdot[CH_2]_2\cdot CH(CH_3)\cdot CH_2\cdot CO_2H \text{ (2 : 6-\textit{Dimethyl}-2-\textit{octenoic}-8 \textit{acid}).}$$

It is a liquid boiling at 152° under 18 mm. pressure, has a faint odour of capric acid and is obtained by the oxidation of *citronellal* (an aldehyde, $C_{10}H_{18}O$, abundant in ethereal oils).

One of the two formulæ must be attributed to Rhodinic Acid (lævo-rotatory), obtained by oxidising *rhodinol*, $C_{10}H_{20}O$.

An inactive i-Rhodinic Acid is also known, this being obtained by the reduction (sodium in amyl alcohol) of *geranic acid*, $(CH_3)_2:C:CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CO_2H$, the hydrogen being added only at the $\alpha\beta$-double linking.

UNDECENOIC ACID, $CH_2:CH\cdot[CH_2]_8\cdot CO_2H$. The position of the double linking in this acid is confirmed by the fact that, on oxidation, the acid yields considerable quantities of Sebacic Acid, $CO_2H\cdot[CH_2]_8\cdot CO_2H$.

It is obtained (about 10 per cent.) on distilling castor oil under reduced pressure. It forms crystals melting at 24·5° and boils unchanged at 213·5° (100 mm.). When reduced with hydrogen iodide, it gives normal undecoic acid, the non-branched character of the carbon atom chain being thus proved.

HYPOGÆIC ACID, $CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_5\cdot CO_2H$, was formerly thought to exist in *Arachis hypogœa*, but the acid there present has been shown to be another acid (arachic acid). It may be prepared by fusing stearolic acid with potash, an intermediate product with two double bonds being probably formed:

$$\underset{\text{Stearolic acid}}{CH_3\cdot[CH_2]_7\cdot C\,\vdots\,C\cdot[CH_2]_5\cdot CH_2\cdot CH_2\cdot CO_2H} \rightarrow$$

$$\underset{\text{Hypothetical intermediate acid}}{CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_5\cdot CH:CH\cdot CO_2H} \rightarrow$$

$$\underset{\text{Acetic acid}}{CH_3\cdot CO_2H} + \underset{\text{Hypogæic acid}}{CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_5\cdot CO_2H}.$$

OLEIC ACID, $C_{18}H_{34}O_2$

$(CH_3\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H)$

This acid is very abundant in nature in the form of glyceride (*triolein*), especially in vegetable and animal oils and fats. After hydrolysis of the fat, the fatty acids are liberated and from these the oleic acid separates, as it is liquid, whilst the others are solid. Although Chevreul discovered oleic acid at the beginning of the nineteenth century, it was only in 1846 that its composition was definitely established by Gottlieb.

In the subsequent section dealing with soap and candles, the method of preparing commercial oleic acid or "oleine" on a large scale will be described in detail; at the present juncture, only the constitution and the methods of obtaining *pure* oleic acid will be considered. Oils rich in olein (olive oil, almond oil, lard, etc.) are hydrolysed with caustic potash in the hot, the fatty acids being separated from the transparent soap thus obtained by means of hydrochloric acid; these acids are then heated for several hours with lead oxide at 100°, and the resulting lead salts dried and extracted with ether. This solvent dissolves only the lead oleate, the oleic acid being freed from the lead by means of hydrochloric acid. The oleic acid thus obtained is purified by transforming it into the barium salt and crystallising this from dilute alcohol, or by repeatedly freezing (at − 6°, − 7°) and squeezing the solid oleic acid, which, when pure, melts at 14° and has the specific gravity 0·900 in the liquid state; it has neither smell nor taste and, in alcoholic solution, shows no reaction towards litmus. In the air and when kept for a long time, the acid turns brown, assumes an acid reaction and taste, and undergoes partial oxidation. Under a pressure of 10 mm., it boils unchanged at 223°; it may also be distilled without alteration by means of steam superheated at 250°.

The *salts* of oleic acid (and of other high fatty acids) form the *soaps;* the alkali salts are soluble in water and separable from this by salt (NaCl), in saturated solutions of which they are completely insoluble. The calcium, barium, lead, etc., salts or soaps are insoluble in water.

The action of concentrated sulphuric acid is mentioned later (*see* Iso-oleic Acid).

An important and characteristic reaction of oleic acid is its almost quantitative transformation, by a little nitrous acid (also by heating at 200° with sulphurous acid or sodium bisulphite), into the stereoisomeric Elaidic Acid, which separates from alcoholic solution in white scales melting at 51° to 52° and boiling unchanged at 225° under a pressure of 10 mm.[1]

That these two isomeric acids have direct (normal) carbon-atom chains is shown with certainty by the fact that, on reduction (*e. g.*, with hydriodic acid and phosphorus or directly with hydrogen, as in the industrial hardening of oils : *see later*, section on Hydrolysis of Fats), each of them takes up two hydrogen atoms giving stearic acid, which is known to have an unbranched carbon-atom chain; also with bromine, they give dibromo-derivatives of stearic acid, and, with permanganate, *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$.[2]

ISO-OLEIC ACID, $C_{18}H_{34}O_2$. With concentrated sulphuric acid, elaidic and oleic acids give Stearinsulphuric Acid, $C_{17}H_{34}(O\cdot SO_3H)\cdot CO_2H$, which, with hot water, loses sulphuric acid and gives *hydroxystearic acid*, $C_{17}H_{34}(OH)\cdot CO_2H$ (with the OH at the position 10). When distilled under reduced pressure (100 mm.) or with superheated steam, this acid loses water and gives a considerable quantity of a white, solid acid—*iso-oleic acid*—which is readily soluble in alcohol and slightly so in ether, from which it crystallises in plates, melting at 44° to 45°. The addition of the molecule of water to oleic or elaidic acid should take place at the central double linking (provided the sulphuric acid does not previously displace this linking) and the subsequent separation of water should occur at two carbon atoms adjacent to the double linking, so that the probable constitution of iso-oleic acid is, $CH_3\cdot[CH_2]_8\cdot CH:CH\cdot[CH_2]_6\cdot CO_2H$. Various facts are, however, known which throw doubt on the accuracy of this formula.

$\Delta^{\alpha\beta}$-OLEIC ACID (2-Octadecenoic-1 Acid), $CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot CO_2H$, is

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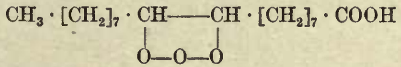
[1] From an industrial point of view the transformation of a liquid fatty acid into a solid one is of interest. but this change is not utilisable in practice as it proceeds well only with fairly pure and fresh oleic acid, and not with the commercial acid, which may be old and possibly polymerised (*see also later*, section on Hydrolysis of Fats).

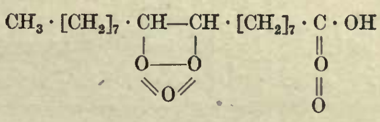
[2] The position of the double linking in the molecule was under discussion for a number of years, and until quite recently this linking was held to be at the end of the chain next the carboxyl group, *i. e.*, in the $\alpha\ \beta$-position, $CH_3\cdot[CH_2]_{14}\cdot CH:CH\cdot COOH$, since fusion of these two acids with caustic potash resulted in the formation of palmitic acid (*Varrentrapp's reaction*, p. 350). This proof no longer seemed sufficient, however, when it was shown that fusion with potash generally displaced the double bond. On the other hand, *Baruch* (1894) succeeded in eliminating hydrogen bromide from the dibromide of oleic acid, thus obtaining stearolic acid, which has a triple bond in the middle of the molecule. Also the products of oxidation (by permanganate) of oleic acid consist partly of pelargonic and azelaic acids, which contain nine carbon atoms, this reaction hence indicating that the oleic acid molecule breaks in the middle of the chain, at the position of the double linking.

The most certain proof of the constitution of oleic acid has been advanced only recently as a result of the study of the *ozonide of oleic acid* and of its decomposition products (E. Molinari and Soncini, 1905 and 1906; C. Harries, 1906). The ozone is added quantitatively at the position of the double bond (*see* p. 107), and, according as ozonised air (E. Molinari) or ozonised oxygen (Harries) is employed, so the simple ozonide :



$$\begin{array}{l} CH_3\cdot[CH_2]_7\cdot CH\text{——}CH\cdot[CH_2]_7\cdot COOH \\ \qquad\qquad\qquad\quad\ |\qquad\quad\ | \\ \qquad\qquad\qquad\quad O\text{—}O\text{—}O \end{array}$$

or a peroxide of the ozonide :



$$\begin{array}{l} CH_3\cdot[CH_2]_7\cdot CH\text{—}CH\cdot[CH_2]_7\cdot C\cdot OH \\ \qquad\qquad\qquad\quad\ |\qquad\ |\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad O\text{——}O\qquad\qquad\ \ O \\ \qquad\qquad\qquad\qquad \diagdown O \diagup \qquad\qquad\ \ \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\ O \end{array}$$

is obtained.

Decomposition of these *ozonides* (of oleic and elaidic acids) with dilute alkali or water in the hot results in the formation of acids (nonoic, azelaic, and others) or aldehydes (nonyl and semiazelaic) with nine carbon atoms, showing that the molecule is ruptured at the position of the central double linking.

prepared by the removal of 1 mol. of halogen hydracid from the α-halogen derivative of stearic acid. It forms white crystals melting at 58° to 59°, does not take up ozone in cold chloroform solution, and gives palmitic acid when treated with permanganate.

ERUCIC ACID (9-Docosenoic-22 Acid), $CH_3 \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_{11} \cdot CO_2H$, is found as glyceride in the oils of black and white mustard, and in those of grape-seed and ravison, from which it is readily extracted. It is obtained crystalline from alcohol in shining needles melting at 34°, and boils at 254·5° under a pressure of 10 mm.

It forms a lead salt soluble in hot ether, as does oleic acid, and, like the latter, it is readily transformed into its stereoisomeride, Brassidic Acid, by the action of a little nitrous acid or of sulphurous or hydrobromic acid in glacial acetic acid solution. This isomeride crystallises from alcohol in leaflets melting at 65°, and boils at 256° under a pressure of 10 mm.; its lead salt is slightly soluble in hot ether.

These two isomerides are not reduced by sodium amalgam, but with hydriodic acid they yield the saturated behenic acid, $C_{22}H_{44}O_2$. When fused with potash, they give arachic ($C_{20}H_{40}O_2$) and acetic acids. They yield various oxidation, bromination, and esterification products. They have normal carbon-atom chains and the position of the double linking is indicated by the fact that *nonoic acid*, $CH_3 \cdot [CH_2]_7 \cdot COOH$, and *brassylic acid*, $CO_2H \cdot [CH_2]_{11} \cdot CO_2H$ (and also a little arachic acid), are among the products of oxidation by nitric acid, while elimination of HBr from the dibrominated product gives the corresponding *behenolic acid*, which has a triple bond and is of known constitution.

ISOERUCIC ACID, $CH_3 \cdot [CH_2]_8 \cdot CH : CH \cdot [CH_2]_{10} \cdot CO_2H$ (?), is obtained by adding hydrogen iodide to, and then removing it from, erucic acid (just as with *iso-oleic acid*), and it appears that the double linking is not displaced during these changes, since decomposition of the dibromide of this acid (*i. e.*, elimination of HBr) gives the same behenolic acid as is given by erucic acid, while oxidation with nitric acid also gives nonoic and brassylic acids. Isoerucic acid should hence have the same constitution as erucic and brassidic acids, so that, contrary to theoretical indications, three isomerides would seem to exist; this requires confirmation. This acid melts at 54° to 56°.

B. UNSATURATED MONOBASIC ACIDS OF THE SERIES, $C_nH_{2n-4}O_2$

The members of this series may be divided into two groups, as is the case with the hydrocarbons of the diolefine and acetylene series (*see* p. 109): acids having a triple linking (propiolic series) and those having two double linkings (diolefine series).

(*a*) ACIDS WITH TRIPLE LINKING

(Propiolic or Acetylenecarboxylic Series)

Name	Constitutional formula	Melting-point	Boiling-point
$C_3H_2O_2$ Acetylenecarboxylic (*propiolic*) acid	$HC \vdots C \cdot CO_2H$	9°	83° (50 mm.)
$C_4H_4O_2$ Methylacetylenecarboxylic (*tetrolic*) acid	$CH_3 \cdot C \vdots C \cdot CO_2H$	76·5°	203°
$C_5H_6O_2$ Ethyl-acetylenecarboxylic acid .	$C_2H_5 \cdot C \vdots C \cdot CO_2H$	50°	—
$C_6H_8O_2$ Propyl- ,, ,, .	$C_3H_7 \cdot C \vdots C \cdot CO_2H$	27°	125° (20 mm.)
$C_6H_8O_2$ Isopropyl- ,, ,, .	$C_3H_7 \cdot C \vdots C \cdot CO_2H$	38°	115° ,,
$C_7H_{10}O_2$ n-Butyl- ,, ,, .	$C_4H_9 \cdot C \vdots C \cdot CO_2H$	—	135° ,,
$C_7H_{10}O_2$ tert.-Butyl- ,, ,, .	$C_4H_9 \cdot C \vdots C \cdot CO_2H$	47°	116° ,,
$C_8H_{12}O_2$ n-Amyl- ,, ,, .	$C_5H_{11} \cdot C \vdots C \cdot CO_2H$	5°	149° ,,
$C_9H_{14}O_2$ n-Hexyl- ,, ,, .	$C_6H_{13} \cdot C \vdots C \cdot CO_2H$	−10°	—
$C_{10}H_{16}O_2$ n-Heptyl- ,, ,, .	$C_7H_{15} \cdot C \vdots C \cdot CO_2H$	6°–10°	166° (20 mm.)
$C_{12}H_{20}O_2$ n-Nonyl- ,, ,, .	$C_9H_{19} \cdot C \vdots C \cdot CO_2H$	30°	—
$C_{11}H_{18}O_2$ Dehydroundecenoic acid . .	$CH \vdots C \cdot [CH_{28}] \cdot CO_2H$	42·8°	175° (15 mm.)
$C_{11}H_{18}O_2$ Undecolic acid	$CH_3 \cdot C \vdots C[CH_2]_7 \cdot CO_2H$	59·5°	—
$C_{18}H_{32}O_2$ Stearolic acid	$CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H$	48°	—
$C_{18}H_{32}O_2$ Tariric acid	$CH_3 \cdot [CH_2]_{10} \cdot C \vdots C \cdot [CH_2]_4 \cdot CO_2H$	50·5°	—
$C_{22}H_{40}O_2$ Behenolic acid	$CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_{11} \cdot CO_2H$	57·5°	—

PREPARATION. These acids may be obtained by the following reactions:

From a sodium alkyl acetylide (suspended in ether), by the action of CO_2 (*a*) or of ethyl chloroformate (*b*):

(*a*) $CH_3 \cdot C \vdots C \cdot Na + CO_2 = \underset{\text{Sodium methylpropiolate}}{CH_3 \cdot C \vdots C \cdot CO_2Na}.$

(*b*) $C_3H_7 \cdot C \vdots C \cdot Na + Cl \cdot CO \cdot OC_2H_5 = NaCl + \underset{\text{Ethyl propylacetylenecarboxylate}}{C_3H_7 \cdot C \vdots C \cdot CO \cdot OC_2H_5}.$

Various other acids of this series having the triple linking at a distance from the carboxyl group (and hence much more stable than the preceding, which, when heated, lose CO_2 and give acetylene hydrocarbons) are obtained by the elimination of 2HBr (by the action of alkali) from acids of the oleic series, this reaction being similar to that taking place with unsaturated hydrocarbons (*see* p. 110):

$$\underset{\text{Dibromide of oleic acid}}{CH_3 \cdot [CH_2]_7 \cdot CHBr \cdot CHBr \cdot [CH_2]_7 \cdot CO_2H} =$$
$$2HBr + \underset{\text{Stearolic acid}}{CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H}.$$

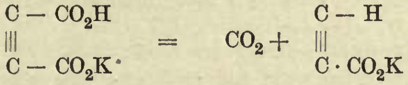
PROPERTIES. Acids of the type $R \cdot C \vdots C \cdot CO_2H$, when treated with sodium in absolute alcoholic solution, take up 4 atoms of hydrogen, giving acids of the saturated series; they also combine easily with 2 atoms of bromine, but the second pair of bromine atoms, required to produce saturation, are added only with difficulty (the action of light facilitates the reaction); when boiled with *alcoholic* potash, they take up a molecule of water, forming saturated β-ketonic acids:

$$R \cdot C \vdots C \cdot CO_2H + H_2O = R \cdot CO \cdot CH_2 \cdot CO_2H;$$

with aqueous potash, however, they yield methyl ketones, $R \cdot CO \cdot CH_3$, separation of CO_2 also taking place; tert.-butyltetrolic acid does not react. The amines and hydrazine also give characteristic reactions with these acids. The esters of the acids have pleasant odours and are used in perfumes.

Acids with a triple bond do not unite with the ozone of a current of ozonised *air* (E. Molinari, 1907 and 1908), but yield peroxyozonides with ozonised *oxygen* (Harries, 1907; *see* p. 359).

PROPIOLIC ACID (Propinoic, Propargylic, or Acetylenecarboxylic Acid), $CH \vdots C . CO_2H$, is obtained by heating the aqueous solution of potassium acetylenedicarboxylate:



$$\begin{array}{c} C - CO_2H \\ \vert\vert\vert \\ C - CO_2K \end{array} = CO_2 + \begin{array}{c} C - H \\ \vert\vert\vert \\ C \cdot CO_2K \end{array}$$

Propiolic acid is a liquid with a more intense odour than acetic acid; it has the sp. gr. 1·139, is soluble in water, alcohol, or ether, solidifies at 4°, melts at 9°, and distils unchanged at a pressure of 50 mm.

The alkali and alkaline-earth salts are extremely soluble in water.

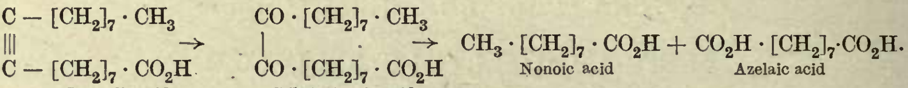
From its esters, metallic *acetylides* (p. 112) are readily prepared. Under the action of light and in a vacuum, it undergoes partial polymerisation, yielding benzenetricarboxylic acid.

TETROLIC ACID (2-Butinoic or Methylpropiolic Acid), $CH_3 \cdot C \vdots C \cdot CO_2H$, is obtained by eliminating HCl from the β-chloro-derivative of crotonic or isocrotonic acid. It crystallises from water in rhombic plates, melting at 76·5° and boils unchanged at 203°, but it distils only with difficulty in a current of steam.

Under the action of sodium in alcoholic solution (but not with sodium amalgam in aqueous solution), it takes up hydrogen with formation of butyric acid. When oxidised with permanganate in alkaline solution, it yields acetic and oxalic acids.

DEHYDROUNDECENOIC ACID (1-Undecinoic-11 Acid), $HC \vdots C \cdot [CH_2]_8 \cdot CO_2H$, obtained by heating dibromoundecenoic acid with alcoholic potash, melts at 42·8°. On oxidation, it forms sebacic acid, $CO_2H \cdot [CH_2]_8 \cdot CO_2H$. It readily forms acetylides. Treatment with alcoholic potash at 180° converts it into the isomeric Undecolic Acid (2-*undecinoic*-11 *acid*), $CH_3 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H$, melting at 59·5°; the latter is hence formed with the dehydroundecenoic acid, if the reaction referred to above takes place at a high temperature. Oxidation of undecolic acid yields azelaic acid, $CO_2H \cdot [CH_2]_7 \cdot CO_2H$; it does not give acetylides, owing to the absence of the characteristic acetylenic hydrogen atom (*see* p. 110).

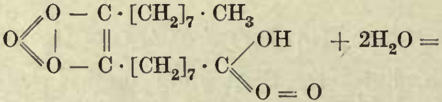
STEAROLIC ACID (9-Octadecinoic-1 Acid), $CH_3 \cdot [CH_2]_7 \cdot C \vdots C \cdot [CH_2]_7 \cdot CO_2H$, is readily obtained by boiling dibromostearic acid (prepared by brominating oleic or elaidic acid) with alcoholic potash. It melts at 48°, and under the influence of sulphuric acid takes up water, giving a ketostearic acid. When oxidised with permanganate, it takes up 2 atoms of oxygen, giving diketostearic acid, whilst with nitric acid it is resolved into nonoic and azelaic acids (it is, however, stable in the air, and thus differs from oleic and linolic acids):



$$\underset{\text{Stearolic acid}}{\begin{array}{l} C - [CH_2]_7 \cdot CH_3 \\ ||| \\ C - [CH_2]_7 \cdot CO_2H \end{array}} \rightarrow \underset{\text{Diketostearic acid}}{\begin{array}{l} CO \cdot [CH_2]_7 \cdot CH_3 \\ | \\ CO \cdot [CH_2]_7 \cdot CO_2H \end{array}} \rightarrow \underset{\text{Nonoic acid}}{CH_3 \cdot [CH_2]_7 \cdot CO_2H} + \underset{\text{Azelaic acid}}{CO_2H \cdot [CH_2]_7 \cdot CO_2H}.$$

Stearolic acid unites with 2HI, and the resulting diiodostearic acid, when heated with alcoholic potash, gives stearolic acid again, but in two isomeric forms, having the triple linking in the 8 to 9 and 10 to 11 positions respectively.

The constitution of stearolic acid was confirmed by Harries (1907) by decomposing the peroxyozonide of the acid, obtained by the action of *ozonised oxygen* (ozonised air does not yield an ozonide, *see* pp. 107, 359):



Peroxyozonide of stearolic acid

$$+ 2H_2O =$$

$$H_2O_2 + \underset{\text{Nonoic acid}}{CH_3 \cdot [CH_2]_7 \cdot CO_2H} + \underset{\text{Azelaic acid}}{CO_2H \cdot [CH_2]_7 \cdot CO_2H}.$$

TARIRIC ACID (6-Octadecinoic-1 Acid), $CH_3 \cdot [CH_2]_{10} \cdot C \vdots C \cdot [CH_2]_4 \cdot CO_2H$, is isomeric with stearolic acid and melts at 50·5°; as glyceride, it forms the principal component of the fat of the fruit of *Picramnia camboita.* It is the first compound with a triple bond resulting from the vital process of an organism. It is stable in the air and yields stearic acid on reduction with hydriodic acid, so that its molecule contains a normal carbon atom chain. Energetic oxidation with permanganate or nitric acid yields *lauric acid,* $CH_3 \cdot [CH_2]_{10} \cdot CO_2H$, and *adipic acid,* $CO_2H \cdot [CH_2]_4 \cdot CO_2H$.

BEHENOLIC ACID (9-Docosinoic-22 Acid), $CH_3 \cdot [CH_2]_7 \cdot C \vdots [CH_2]_{11} \cdot CO_2H$, melting at 57·5°, is obtained from the dibromide of erucic or brassidic acid, in the same way as stearolic acid is formed from oleic acid. Its constitution follows from its behaviour towards reducing and oxidising agents and from the transformation of its oxime (Beckmann).

(*b*) ACIDS WITH TWO DOUBLE BONDS, $C_nH_{2n-4}O_2$

(Diolefinic or Sorbinic Series)

These acids are prepared synthetically by methods analogous to those used for obtaining *αβ*-unsaturated acids, for example, by treating *αβ*-unsaturated aldehydes with malonic acid in presence of pyridine:

$$\underset{\text{Acroleïn}}{CH_2 : CH \cdot CHO} + CO_2H \cdot CH_2 \cdot CO_2H =$$

$$CO_2 + H_2O + \underset{\beta\text{-Vinylacrylic acid}}{CH_2 : CH : CH : CH \cdot CO_2H}.$$

The acids of the sorbinic series, in which the two double linkings are *conjugated*—that is, one in the *αβ*- and the other in the *γδ*-position and therefore separated by a simple linking—may be reduced by sodium amalgam in aqueous solution (in presence of a stream of CO_2 to fix the alkali); only two hydrogen atoms are then added, one for each double linking, and a new double linking remains in the place of the simple linking previously separating the two original double bonds :

$$X \cdot CH : CH \cdot CH : CH \cdot CO_2H + H_2 = X \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO_2H.$$

When these sorbinic acids are oxidised with permanganate, two hydroxyl groups enter at the $\alpha\beta$-double linking, while the chain is broken at the $\gamma\delta$-double linking with formation of an aldehyde (which then undergoes oxidation) and racemic acid :

$$X \cdot CH : CH \cdot CH : CH \cdot CO_2H \rightarrow X \cdot CHO + \underset{\text{Racemic acid}}{CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2H}.$$

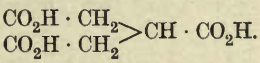
When they are heated with aqueous ammonia, 2 mols. of the latter are added at the double linking and two diamino-acids formed.

On heating, acids of the sorbinic series readily polymerise; hence, when they are heated with lime or baryta, not only is CO_2 removed and diolefine hydrocarbons obtained, but di- and tri-molecular condensation occurs, giving more complex hydrocarbons which are probably of cyclic structure.

β-VINYLACRYLIC ACID (1 : 3-Pentadienoic Acid), $CH_2 : CH \cdot CH : CH \cdot CO_2H$, is synthesised by the method given above. It forms prisms showing a grey reflex, and dissolves slightly in cold water, but readily in hot. At 80° it melts to a mobile liquid, which, at 100° to 115°, becomes dense and syrupy and then suddenly decomposes with evolution of gas. In carbon disulphide solution it unites with four atoms of bromine.

SORBINIC or **SORBIC ACID** (2 : 4-Hexadienoic Acid), $CH_3 \cdot CH : CH \cdot CH : CH \cdot CO_2H$, occurs in considerable quantities in mountain-ash berries. It melts at 134·5°, boils at 228° with partial decomposition, is odourless and dissolves readily in alcohol or ether.

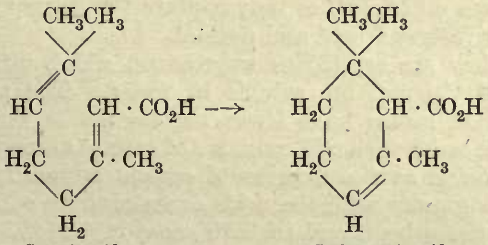
DIALLYLACETIC ACID (1 : 6-Heptadiene-4-methyloic Acid), $CH_2 : CH \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH : CH_2$, is obtained synthetically from acetoacetic acid by two separate introductions of the allyl residue. It is a liquid, sp. gr. 0·950, b.-pt. 219° to 222°, and has an unpleasant smell. Oxidation with nitric acid leads to the rupture of the carbon atom chain at the two double linkings and formation of *tricarballylic acid :*



$$\begin{matrix} CO_2H \cdot CH_2 \\ CO_2H \cdot CH_2 \end{matrix} > CH \cdot CO_2H.$$

GERANIC ACID (2 : 6-Dimethyl-2 : 6-octadienoic-8 Acid), $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CO_2H$, is obtained either by oxidation of the corresponding aldehyde (*citral*) with silver oxide, or by elimination of water from citraloxime by the action of acetic anhydride and hydrolysis of the resulting nitrile with alcoholic potash. It has also been obtained, by a series of reactions, from *methylheptenone*, $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$.

It is a colourless liquid of not very pleasing odour and boils at 153° under a pressure of 13 mm. When shaken with 70 per cent. sulphuric acid it yields, among other products, the isomeric *α-cyclogeranic acid,* melting at 106° :



Geranic acid α-Cyclogeranic acid

LINOLIC ACID, $C_{18}H_{32}O_2$. In the form of glyceride, this acid is an important constituent of *drying oils* (linseed, sunflower-seed, etc.). From these oils a mixture of unsaturated fatty acids may be obtained which gives the nitrous acid reaction (solidification, owing to the formation of elaidic from oleic acid) only to a slight degree; it contains less hydrogen, but not less carbon than oleic acid, and is readily oxidised and thickened by the oxygen of the air. The salts of these drying acids are still more readily oxidisable than the acids themselves, and their lead salts, like that of oleic acid, are soluble in ether. The various components of this mixture of fatty acids—with two or three double linkings —have not been completely separated, but as they fix 2 mols. of ozone (Molinari and Soncini, 1905), give a *tetrabromostearic acid*, $C_{18}H_{32}O_2Br_4$, with bromine, and with alkaline permanganate yield a *tetrahydroxystearic* (*sativic*) *acid*, $C_{18}H_{32}O_2(OH)_4$, which gives stearic acid with hydrogen iodide, the mixture must contain an acid with two double bonds. This is linolic acid, $C_{18}H_{32}O_2$, which has not been obtained pure, although its stereoisomerides—α-Elæostearic Acid, melting at 43° to 44°, and Telfairic Acid, obtained from telfairia oil, m.-pt. 6° and b.-pt. 220° to 225° under 13 mm. pressure—have been prepared crystalline. Distillation of ricinelaidic acid gives a further isomeride, which has a normal structure, contains two double linkings, and melts at 53° to 54°.

(*c*) ACIDS WITH THREE DOUBLE BONDS, $C_nH_{2n-6}O_2$

CITRYLIDENEACETIC ACID (2 : 6-Dimethyl - 2 : 6 : 8-decatrienoic-10 Acid), $CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH . CH : CH . CO_2H$, is a mobile oil, distilling at 175° under a pressure of 18 mm., and is formed by condensing 1 mol. of citral with 1 mol. of malonic acid in presence of pyridine:

$$\underbrace{CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CHO}_{\text{Citral}} + \underbrace{CO_2H \cdot CH_2 \cdot CO_2H}_{\text{Malonic acid}} =$$

$$H_2O + CO_2 + \underbrace{C_{12}H_{18}O_2}_{\text{Citrylideneacetic acid}}.$$

LINOLENIC AND ISOLINOLENIC ACIDS, $C_{18}H_{30}O_2$, are components of the mixture of drying acids referred to above, but have not yet been isolated in a pure state. With bromine, however, two *hexabromostearic acids*, $C_{18}H_{30}O_2Br_6$, and with permanganate two *hexahydroxystearic acids*, $C_{18}H_{30}O_2(OH)_6$, have been obtained, and these must be derived from two acids containing three double bonds. The fatty acids of linseed oil contain 50 per cent. of these two acids, together with linolic and oleic acids, whilst the other drying oils contain linolic acid in preponderating amount.

The constitution of Linolenic Acid was definitely established by E. Erdmann, Bedford, and Raspe (1909) by decomposing the corresponding tri-ozonides. The three double bonds occur in a normal chain:

$$CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H.$$

The ozonides of two stereoisomerides were prepared, their products of decomposition being: propaldehyde, malonic dialdehyde, and azelaic semialdehyde.

Fish oil contains another isomeride, Jecorinic Acid, $C_{18}H_{30}O_2$, which has been little studied.

III. POLYBASIC FATTY ACIDS

A. SATURATED DIBASIC ACIDS, $C_nH_{2n}(CO_2H)_2$

These acids are dibasic, since they contain two carboxyl groups and form two series of derivatives: acid and normal.

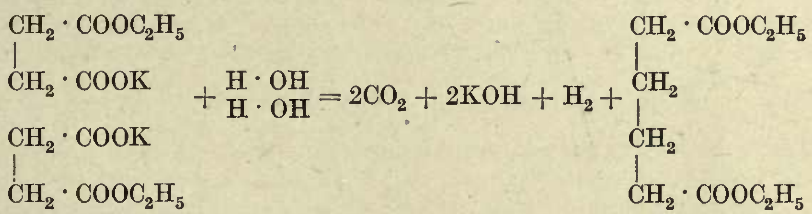
In general they are crystalline substances, which distil unchanged in a vacuum (beyond C_3) and are soluble in water. The members with even numbers of carbon atoms have lower melting-points than their immediate neighbours in the series with odd numbers of carbon atoms, and the differences thus shown diminish as the number of carbon atoms increases. The solubility in water is greater with the acids containing an odd number of carbon atoms than for the others, and in both cases it diminishes with increase of molecular weight. The dissociation constant is very high for oxalic acid, and diminishes considerably in the higher homologues, which are hence less energetic acids.

TABLE OF THE NORMAL SATURATED DIBASIC ACIDS

Empirical formula	Name	Structural formula	Melting-point
$C_2H_2O_4$	Oxalic acid	$COOH \cdot COOH$	189° (anhyd.)
$C_3H_4O_4$	Malonic „	$CO_2H \cdot CH_2 \cdot CO_2H$	132°
$C_4H_6O_4$	Succinic „	$CO_2H \cdot [CH_2]_2 \cdot CO_2H$	182°
$C_5H_8O_4$	Glutaric „	$CO_2H \cdot [CH_2]_3 \cdot CO_2H$	97·5°
$C_6H_{10}O_4$	Adipic „	$CO_2H \cdot [CH_2]_4 \cdot CO_2H$	149°
$C_7H_{12}O_4$	Pimelic „	$CO_2H \cdot [CH_2]_5 \cdot CO_2H$	103°
$C_8H_{14}O_4$	Suberic „	$CO_2H \cdot [CH_2]_6 \cdot OC_2H$	141°
$C_9H_{16}O_4$	Azelaic „	$CO_2H \cdot [CH_2]_7 \cdot CO_2H$	106°
$C_{10}H_{18}O_4$	Sebacic „	$CO_2H \cdot [CH_2]_8 \cdot CO_2H$	133°
$C_{12}H_{22}O_4$	Decamethylenedicarboxylic acid .	$CO_2H \cdot [CH_2]_{10} \cdot CO_2H$	125°
$C_{13}H_{24}O_4$	Brassylic acid	$CO_2H \cdot [CH_2]_{11} \cdot CO_2H$	112°
$C_{14}H_{26}O_4$	Dodecamethylenedicarboxylic acid	$CO_2H \cdot [CH_2]_{12} \cdot CO_2H$	123°
$C_{17}H_{32}O_4$	Roccellic acid	$CO_2H \cdot [CH_2]_{15} \cdot CO_2H$	132°

METHODS OF PREPARATION. In addition to the usual methods of oxidising monobasic fatty acids, primary hydroxy-acids, alcohols, and glycols, an important and general method consists in hydrolysing the nitriles (*see* p. 238) or cyano-derivatives of the acids, these being obtained from halogen alkyls with a less number of carbon atoms.

Dibasic acids—always of higher molecular weight—are also obtained by the condensation of 2 mols. of the esterified monopotassium salt of a lower dibasic acid by electrolysis of Hofer's apparatus :

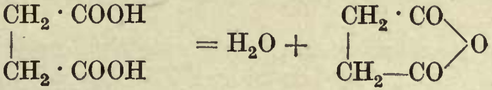


$$\begin{array}{l} \mathrm{CH_2 \cdot COOC_2H_5} \\ | \\ \mathrm{CH_2 \cdot COOK} \\ \\ \mathrm{CH_2 \cdot COOK} \\ | \\ \mathrm{CH_2 \cdot COOC_2H_5} \end{array} + \begin{array}{l} \mathrm{H \cdot OH} \\ \mathrm{H \cdot OH} \end{array} = 2CO_2 + 2KOH + H_2 + \begin{array}{l} \mathrm{CH_2 \cdot COOC_2H_5} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2 \cdot COOC_2H_5} \end{array}$$

2 mols. Potassium ethyl succinate

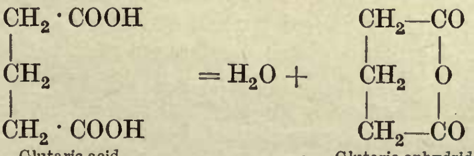
Ethyl adipate

PROPERTIES. The constitution is deduced from the synthesis in which compounds, especially the nitriles, of known constitution are employed. Structural isomerism commences with the acids containing four carbon atoms. Those acids which have the two carboxyls united to different carbon atoms (*i. e.*, other than oxalic and malonic acids and their derivatives), in presence of dehydrating substances (PCl_5, $COCl_2$, etc.), or on heating, lose a molecule of water and form a kind of cyclic compound, known as an *internal anhydride :*



Succinic acid

Succinic anhydride

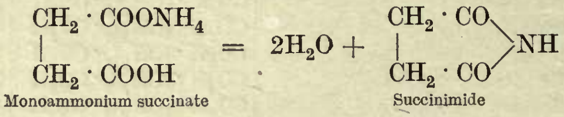


Glutaric acid

Glutaric anhydride

The ready formation of these anhydrides by the reaction of the two terminal carboxyl groups (ω, ω') is readily explained by arranging the carbon atoms in space (*see* pp. 19 *et seq.*), with their valencies in the directions of the angles of regular tetrahedra. Thus, with *succinic acid*, which contains four carbon atoms, the two hydroxyls of the carboxyl groups are found to be moderately close together (Fig. 251), whilst in *glutaric acid* the two hydroxyls are almost superposed, so that water readily separates, forming a closed ring (Fig. 252).

Similarly the amides (*which see*) or the ammonium salts of these acids readily form *imides* (*see later*), which may be hydrolysed like the amides :



$$\begin{array}{l} CH_2 \cdot COONH_4 \\ | \\ CH_2 \cdot COOH \end{array} = 2H_2O + \begin{array}{l} CH_2 \cdot CO \\ | \\ CH_2 \cdot CO \end{array}\!\!>NH$$

Monoammonium succinate Succinimide

OXALIC ACID (Ethandioic Acid), $\begin{array}{l} COOH \\ | \\ COOH \end{array}$, has been known from the earliest times, since it occurs frequently in nature in plants, especially in *sorrel*, in the form of acid potassium oxalate, and also as incrustations of calcium oxalate in plant-cells and in the roots of rhubarb.

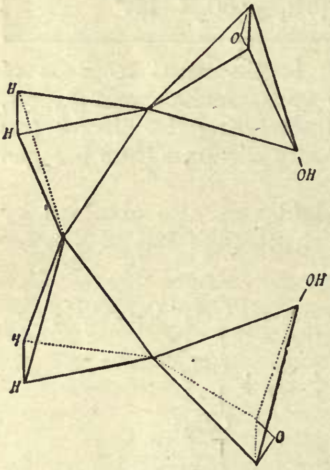


FIG. 251.

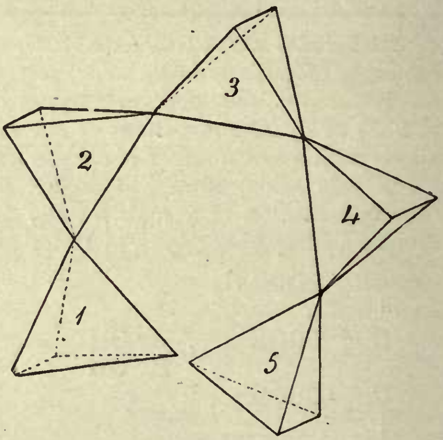


FIG. 252.

It is often formed in the oxidation of organic substances (sugar, wood, starch, etc.) by nitric acid or permanganate, or by fused caustic potash.

It is obtained synthetically by heating sodium or potassium formate rapidly (best in a vacuum at 280°) : $2H \cdot COONa = Na_2C_2O_4 + H_2$ (the reverse change, from oxalic to formic acid, has already been referred to on p. 324), or by passing carbon dioxide over metallic sodium heated to about 350° : $2Na + 2CO_2 = Na_2C_2O_4$.

Its industrial manufacture was, until recently, carried out exclusively by the method devised by Gay-Lussac in 1829 and applied by Dale in 1856 : sawdust (1 part) moistened with caustic potash solution (2 parts, sp. gr. 1·4) or a mixture of 4 parts of KOH and 6 parts of NaOH is heated at about 240° and frequently stirred on iron plates until a greenish-yellow mass is formed. While still hot, this is dissolved in water and the solution filtered and concentrated to 38° Bé. When cold, the solution deposits crude sodium oxalate, which is dissolved in a small quantity of boiling water and precipitated as insoluble calcium oxalate by means of lime. The precipitate is made into a paste with water and the oxalic acid liberated by addition of sulphuric acid. The liquid is decanted and concentrated until the whole of the calcium sulphate separates, the oxalic acid being then allowed to crystallise out and subsequently purified by repeated recrystallisation. When sugar (saccharose) is obtainable at a very low price, it may be oxidised with nitric acid (sp. gr. 1·4) in the cold in presence of 0·1 per cent. of vanadic oxide, V_2O_5, but for the process to pay, the nitrous vapours evolved must be recovered for the regeneration of the nitric acid. From 100 kilos of sugar 140 kilos of oxalic acid may be obtained, while Molinari and Fedeli (1914) obtained more than 160 kilos of the acid (*see also* Naumann, Moeser, and Lindenbaum's Ger. Pat. 183,022, 1907, and Ger. Pat. 208,999).

At the present time, the acid and also the various alkaline oxalates are prepared by Goldschmidt's process (*see* p. 324), which consists in heating a mixture of potassium or sodium formate with a little potassium carbonate in presence of a small proportion of potassium oxalate and a slight excess of alkali (3 to 4 per cent.). According to Ger. Pat. 229,853 of 1908 about 30 parts of sodium formate and 0·3 part of borax or boric acid are heated together at 400° in an iron vessel and well stirred for thirty to forty minutes. Another method of manufacture (Fr. Pat. 413,947, 1910) consists in allowing the formate to fall into an empty pot maintained at 550° to 600° by means of a metal-bath; if the temperature of the mass introduced is kept for half an hour above 400° the formate is converted almost quantitatively into pulverulent oxalate (150 kilos per sq. metre of heated surface); *see also* Kirchner's Ger. Pat. 269,833, 1914. From the oxalate thus obtained the oxalic acid is liberated by means of sulphuric acid (*see above*); the final, somewhat impure mother-liquors may be utilised to make iron oxalate, which, on calcination, yields an excellent English red.

PROPERTIES. Oxalic acid crystallises in odourless, colourless, transparent prisms, $H_2C_2O_4 + 2H_2O$, which have a marked acid taste, effloresce in the air, and have the sp. gr. 1·64. The solubility at various temperatures, expressed as grams of the acid dissolving in 100 grams of water, is as follows :

Temperature .	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Solubility .	5·2	8	13·9	23	35	51·2	75	117·7	204·7	345

The crystals lose their water of crystallisation partly at 30° and completely at 110° to 120°, but melt at 99° in the residual water; the anhydrous acid melts and decomposes at 187° and sublimes at a higher temperature. When heated moderately strongly or treated with concentrated sulphuric acid, oxalic acid decomposes into CO, CO_2, and H_2O. It is somewhat poisonous.

USES. It is used in the dyeing and printing of woollen textiles and yarns; it serves for bleaching straw, removing rust stains from fabrics, purifying glycerine, stearine, tartaric acid, and cream of tartar from the last traces of lime, cleaning brass, etc. To some extent it is used for the manufacture, by electrolytic reduction, of *glycollic acid* (*see later*), which is used in dyeing and printing textiles. Large quantities of the acid are used for the extraction of rare earths from monazite (*see* Vol. I., p. 504).

STATISTICS AND PRICES. Commercial crystallised oxalic acid[1] was sold before the war at 28*s*. to 30*s*. per cwt., while the purified acid cost 40*s*., and the chemically pure 64*s*. During the war the price rose to £20.

The Italian imports of oxalic acid are as follows :

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[1] **Testing of Oxalic Acid.** The acid is estimated by means either of normal caustic soda solution in presence of phenolphthalein, or of decinormal potassium permanganate solution in presence of sulphuric acid in the hot :

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 10CO_2 + 8H_2O + 2MnSO_4.$$

Ammoniacal impurities are detected with Nessler's reagent (Vol. I., p. 690), and, when pure, the acid should leave no ash, and 0·5 gram of it should dissolve completely when shaken with 100 c.c. of ether.

	1908	1910	1912	1913	1914	1915	1916	1917	1918
Cwts. .	1,920	3,780	5,470	5,784	4,104	2,452	1,184	2,958	1,788
Value £	—	6,424	—	8,097	—	8,582	—	50,286	—

The United States imported 1650 tons of oxalic acid in 1911 and 1800 tons in 1913.

In Russia, four factories produced about 850 tons of oxalic acid in 1909, by heating sawdust with alkali. In 1908 Germany exported 5100 tons of oxalic acid and potassium oxalate, 4470 tons (£128,000) in 1909, 5015 tons in 1911, and 5693 tons in 1913.

SALTS OF OXALIC ACID. Owing to the presence of two carboxyl groups in the molecule, oxalic acid gives both acid and neutral salts. The alkaline oxalates are soluble in water and are often used instead of the acid, especially in dyeing.

NORMAL POTASSIUM OXALATE, $K_2C_2O_4$, used to be obtained by neutralising the acid with potassium carbonate, concentrating and allowing to crystallise. Nowadays it is prepared by Goldschmidt's method (*see above*). It dissolves in three parts of water, crystallises with $1H_2O$, and readily effloresces in the air. It costs 42*s*. to 44*s*. per cwt., or, when chemically pure, £3.

ACID POTASSIUM OXALATE (or Potassium Hydrogen Oxalate), KHC_2O_4, is obtained by dissolving the neutral oxalate (1 mol.) and oxalic acid (1 mol.) in water, concentrating and allowing to crystallise, when it separates with $1H_2O$. It has a bitter, acid taste, is poisonous, and dissolves in 14 parts of hot water.

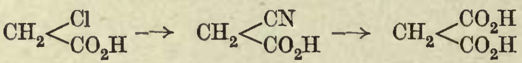
POTASSIUM TETROXALATE (Commercial Salt of Sorrel), $KHC_2O_4 + H_2C_2O_4 + 2H_2O$, does not effloresce or lose its water of crystallisation in the air. It is obtained by mixing a hot, saturated solution of potassium oxalate with the calculated amount of saturated oxalic acid solution. It costs 42*s*. to 44*s*. per cwt., or, if chemically pure, 64*s*.

CALCIUM OXALATE, CaC_2O_4, crystallises with $2H_2O$ and is obtained from a solution of a soluble oxalate, containing either ammonia or acetic acid, by addition of a soluble calcium salt. It is insoluble in water or acetic acid.

FERROUS OXALATE, FeC_2O_4, or, better, **Ferrous Potassium Oxalate, $K_2Fe(C_2O_4)_2 + H_2O$,** gives a yellow aqueous solution owing to the colour of its cation, FeC_2O_4''. It possesses strong reducing properties and is largely used on this account, while it serves also as a good photographic developer.

POTASSIUM FERRIC OXALATE, $K_2Fe_3(C_2O_4)_3$, gives a green aqueous solution owing to the colour of its cation, $Fe(C_2O_4)_3'''$. In the light it yields CO_2 and potassium ferrous oxalate, and it is used in the platinotype method of photography.

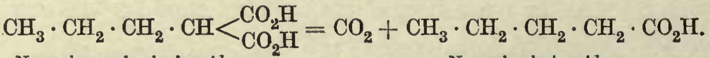
MALONIC ACID (Propandioic Acid), $H_4C_3O_4$ or $CH_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}$, forms crystals melting at 132° and is readily soluble in water (1 : 1·4 at 15°), alcohol, or ether. It occurs in the beetroot and is obtained synthetically by hydrolysing cyanoacetic acid prepared from a hot aqueous solution of potassium chloroacetate and potassium cyanide :



$$CH_2<\begin{matrix}Cl\\CO_2H\end{matrix} \longrightarrow CH_2<\begin{matrix}CN\\CO_2H\end{matrix} \longrightarrow CH_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

Chloroacetic acid Cyanoacetic acid Malonic acid

Like all compounds containing two carboxyl groups united to the same carbon atom, it evolves CO_2 when heated above its melting-point, acetic acid being formed. Higher monobasic acids are similarly obtained from alkylated malonic acids :



$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH<\begin{matrix}CO_2H\\CO_2H\end{matrix} = CO_2 + CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$

Normal propylmalonic acid Normal valeric acid

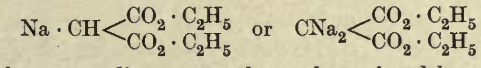
Malonic acid forms an ester, **ETHYL MALONATE, $CH_2<\begin{matrix}CO_2 \cdot C_2H_5\\CO_2 \cdot C_2H_5\end{matrix}$,** which is of great importance, since it allows of the synthetical preparation of the most varied higher dibasic acids, and from these, by loss of carbon dioxide, of the corresponding monobasic acids. This ester is obtained by passing gaseous hydrogen chloride into cyanoacetic acid dissolved in absolute alcohol; it is then separated by distillation, as it boils at 198°. At 15° it has the sp. gr. 1·061.

The hydrogen atoms of the methylene group of this ester may be replaced by one or two atoms of sodium (or halogens) giving highly reactive *sodiomalonic esters*. The sodium in these may be substituted by one or two alkyl groups simply by treatment with an alkyl iodide, sodium iodide being separated at the same time. The resulting products are higher homologues of the malonic ester, and hence yield the corresponding homologues of malonic acid on hydrolysis. The hydrolysis of the esters of dibasic acids by alkali takes place in two stages, the second ester group being hydrolysed more slowly than the first.

HOMOLOGUES OF MALONIC ACID

Name of acid	Formula	Melting-point of acid	Boiling-point of the diethyl ester
Methylmalonic . .	$CH_3 \cdot CH(CO_2H)_2$	about 130°	190°–193°
Dimethylmalonic . .	$(CH_3)_2 : C(CO_2H)_2$	192°–193°	196°
Ethylmalonic . .	$C_2H_5 \cdot CH(CO_2H)_2$	112°	210°
Diethylmalonic . .	$(C_2H_5)_2 : C(CO_2H)_2$	124°	230°
Propylmalonic . .	$C_2H_5 \cdot CH_2 \cdot CH(CO_2H)_2$	93·5°	219°–222°
Dipropylmalonic . .	$(C_2H_5 \cdot CH_2)_2 : C(CO_2H)_2$	156°	248°–250°
Isopropylmalonic . .	$(CH_3)_2 : CH \cdot CH(CO_2H)_2$	86°	213°–214°
Methylethylmalonic .	$(CH_3)(C_2H_5)C(CO_2H)_2$	118°	207°–208°
Butylmalonic . .	$C_2H_5 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H)_2$	98·5°	—
sec. Butylmalonic . .	$C_2H_5 \cdot CH(CH_3) \cdot CH(CO_2H)_2$	76°	224°–225°
Isobutylmalonic . .	$(CH_3)_2 : CH \cdot CH_2 \cdot CH(CO_2H)_2$	107°	225°–226°
Diisobutylmalonic . .	$[(CH_3)_2 : CH \cdot CH_2]_2C(CO_2H)_2$	145°–150°	245°–255°
Methylpropylmalonic .	$(CH_3)(C_2H_5 \cdot CH_2)C(CO_2H)_2$	106°–107°	220°–223°
Methylisopropylmalonic .	$[(CH_3)_2CH](CH_3) : C(CO_2H)_2$	124°	221°
Pentylmalonic . .	$C_2H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H)_2$	82°	—
Isoamylmalonic . .	$(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H)_2$	98°	240°–242°
Diisoamylmalonic . .	$[(CH_3)_2CH \cdot CH_2 \cdot CH_2]_2C(CO_2H)_2$	147°–148°	278°–280°
2-Methylbutylmalonic .	$(CH_3)(C_2H_5)CH \cdot CH_2 \cdot CH(CO_2H)_2$	90°–91°	244°–246°
tert. Amylmalonic . .	$(CH_3)_2(C_2H_5)C \cdot CH(CO_2H)_2$	—	238°
sec. Amylmalonic . .	$(C_2H_5)_2CH \cdot CH(CO_2H)_2$	52°–53°	242°–245°
Methylisobutylmalonic .	$(CH_3)_2CH \cdot CH_2 \cdot C(CH_3)(CO_2H)_2$	122°	230°–235°
Ethylisopropylmalonic .	$(CH_3)_2CH \cdot C(C_2H_5)(CO_2H)_2$	131°–131·5°	232°–233°
Cetylmalonic . . .	$CH_3 \cdot [CH_2]_{15} \cdot CH(CO_2H)_2$	121·5°–122°	—
Dicetylmalonic . .	$[CH_3 \cdot (CH_2)_{15}]_2 : C(CO_2H)_2$	86°–87°	—
Dioctylmalonic . .	$[CH_3 \cdot (CH_2)_7]_2 : C(CO_2H)_2$	75°	338°–340°

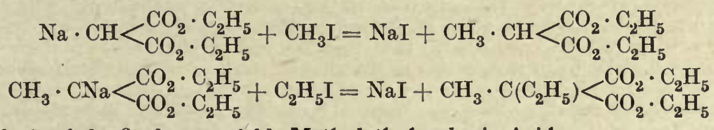
Treatment of ethyl malonate (1 mol.) with sodium (1 or 2 atoms) results in the evolution of hydrogen and the formation of the solid *mono-* or *di-sodiomalonic ester :*



$$\mathrm{Na \cdot CH}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix} \quad \text{or} \quad \mathrm{CNa_2}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix}$$

The sodium of the monosodio-compound may be replaced by an alkyl group and the remaining methylene hydrogen then replaced by sodium, which may subsequently be substituted by an alkyl group different from the first.

An example of this synthesis is as follows (*see also later :* Glutaric Acid):

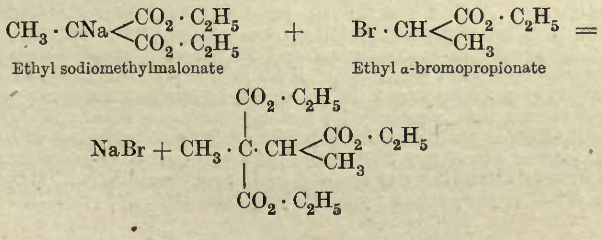


$$\mathrm{Na \cdot CH}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix} + \mathrm{CH_3I} = \mathrm{NaI} + \mathrm{CH_3 \cdot CH}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix}$$

$$\mathrm{CH_3 \cdot CNa}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix} + \mathrm{C_2H_5I} = \mathrm{NaI} + \mathrm{CH_3 \cdot C(C_2H_5)}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix}$$

Hydrolysis of the final ester yields **Methylethylmalonic Acid.**

Homologues of succinic acids may be obtained as follows :

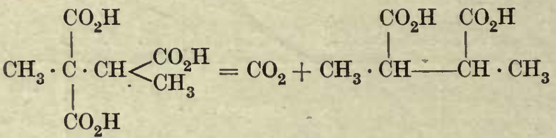


$$\mathrm{CH_3 \cdot CNa}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CO_2 \cdot C_2H_5}\end{matrix} + \mathrm{Br \cdot CH}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CH_3}\end{matrix} =$$

Ethyl sodiomethylmalonate Ethyl α-bromopropionate

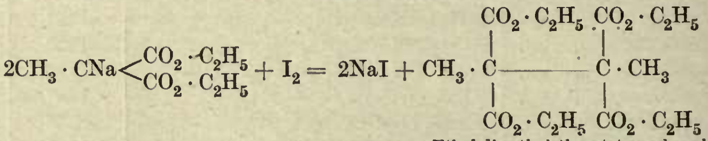
$$\mathrm{NaBr} + \mathrm{CH_3 \cdot} \begin{array}{c}\mathrm{CO_2 \cdot C_2H_5}\\ |\\ \mathrm{C}\\ |\\ \mathrm{CO_2 \cdot C_2H_5}\end{array} \mathrm{\cdot CH}\Big<\begin{matrix}\mathrm{CO_2 \cdot C_2H_5}\\ \mathrm{CH_3}\end{matrix}$$

When this complex ester is saponified and the acid thus formed heated to expel CO_2 from one of the carboxyl groups united to the same carbon atom, symmetrical dimethylsuccinic acid is obtained:



$$CH_3\cdot\overset{CO_2H}{\underset{CO_2H}{C}}\cdot CH\Big<\begin{matrix}CO_2H\\CH_3\end{matrix} = CO_2 + CH_3\cdot\overset{CO_2H}{CH}-\overset{CO_2H}{CH}\cdot CH_3$$

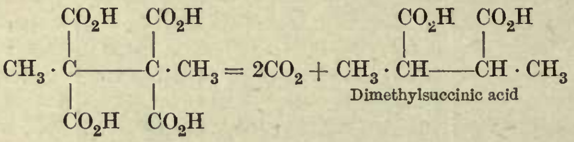
Also 2 mols. of ethyl sodiomethylmalonate (or ethyl sodiomalonate or its homologues) may be condensed in ethereal solution by means of bromine or iodine:



$$2CH_3\cdot CNa\Big<\begin{matrix}CO_2\cdot C_2H_5\\CO_2\cdot C_2H_5\end{matrix} + I_2 = 2NaI + CH_3\cdot\overset{CO_2\cdot C_2H_5}{\underset{CO_2\cdot C_2H_5}{C}}-\overset{CO_2\cdot C_2H_5}{\underset{CO_2\cdot C_2H_5}{C}}\cdot CH_3$$

Ethyl dimethylethanetetracarboxylate

Hydrolysis of this ester gives the corresponding acid and the latter loses $2CO_2$ on heating, yielding dimethylsuccinic acid. Similarly succinic acid may be obtained from ethyl sodiomalonate, and homologous, symmetrical alkylsuccinic acids by condensing 2 mols. of ethyl sodioalkylmalonate containing alkyl groups higher than methyl:



$$CH_3\cdot\overset{CO_2H}{\underset{CO_2H}{C}}-\overset{CO_2H}{\underset{CO_2H}{C}}\cdot CH_3 = 2CO_2 + CH_3\cdot\overset{CO_2H}{CH}-\overset{CO_2H}{CH}\cdot CH_3$$

Dimethylsuccinic acid

SUCCINIC ACIDS, $C_4H_6O_4$ (Two Isomerides)

(*a*) **ORDINARY SUCCINIC ACID** (Butandioic or Ethylenesuccinic Acid), $CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H$, occurs in nature in various plants, in the unripe grape, in certain lignites, and, more especially, in amber, from which it is obtained by distillation or fermentation.[1]

Alcoholic fermentation also yields a small amount of succinic acid, which thus forms a normal constituent of wine. Ehrlich (1909) has shown that, in the alcoholic fermentation of sugar, the succinic acid is formed from the glutamic acid resulting from the decomposition of the cells of the ferment. Numerous syntheses also lead to the formation of succinic acid; *e. g.*, the reduction by hydrogen of fumaric or maleic acid, these being unsaturated dibasic acids, $C_4H_4O_4$; hydrolysis of ethylene cyanide, $CN\cdot CH_2\cdot CH_2\cdot CN$, obtained from ethylene bromide, $C_2H_4Br_2$ (*see above*); reduction of the hydroxy-acids,

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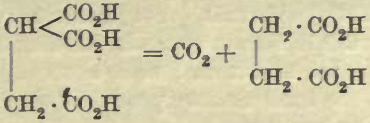
[1] Amber is found on the shores of Denmark and along the coast of the Baltic, in the neighbourhood of Königsberg, Holstein, and Mecklenburg, in Finland, Siberia, and the Urals (Jekaterinenberg), and rarely in Sicily and Spain. It consists of fossil resins (succinite, allingite, beckerite, glessite, gedanite, etc.). That thrown up on to the seashore is transparent, shiny, yellowish, pale (gedanite and succinite) or yellowish-brown (beckerite and stantienite), while that mined is covered with an opaque, hard crust. It is odourless and tasteless, and when rubbed with a cloth becomes electrified. It is insoluble or almost so in ether, cold alcohol and other ordinary solvents, but it gradually dissolves, to the extent of 30 per cent., in boiling alcohol; in chlorhydrin it dissolves somewhat and turns brown. By boiling alkalies it is partially saponified. It softens and swells at 150° to 180°, melts at 250° to 300°, and dry-distils at above 400°, giving succinic acid and *yellow amber oil* (of repulsive smell; sp. gr. 0·95; soluble in alcohol, ether or petroleum ether; used for varnishes) and leaving a residue termed *amber colophony*, used for making varnishes. Amber has the sp. gr. 1·050 to 1·096, the acid value 15 to 34, the saponification number 86 to 150, and the iodine number 57 to 58. It consists of 70 per cent. of the succinic ester of succinoresinol and 28 per cent. of abietinsuccinic acid; sometimes it contains a little sulphur (succinite). It is sometimes adulterated with *copal resin* (which is, however, soluble in various solvents). An excellent substitute for it is *baekelite* (*see* Phenol). Amber is used for ornaments, especially for the mouthpieces of pipes and cigar-holders. Scrap amber is either distilled, or used for making varnish, or softened in the hot with carbon disulphide and pressed, or pressed directly at 200° under 400 atmospheres' pressure to make *block amber*. The output in Prussia before the war was 400 to 450 tons per annum. Italy imported, before the war, 300 to 400 kilos per year at a price varying from £2 to £12 per kilo.

malic and tartaric acids, by means of hydriodic acid; heating of ethyl ethanetricarboxylate above its melting-point:



$$\begin{matrix} CH<^{CO_2H}_{CO_2H} \\ | \\ CH_2\cdot CO_2H \end{matrix} = CO_2 + \begin{matrix} CH_2\cdot CO_2H \\ | \\ CH_2\cdot CO_2H \end{matrix}$$

Various alkylsuccinic acids are obtained by syntheses with ethyl malonate.

HOMOLOGUES OF SUCCINIC ACID

Name of Acid	Composition of acid	Melting-point of acid	Melting point of the anhydride
Methylsuccinic	$C_5H_8O_4$	112°	37°
Ethylsuccinic	$C_6H_{10}O_4$	99°	Liquid
symm. Dimethylsuccinic (fumaroid) . .	$C_6H_{10}O_4$	209°	43°
,, ,, (maleinoid) . .	$C_6H_{10}O_4$	129°	91°
asymm. ,, ...	$C_7H_{12}O_4$	140°–141°	31°
Propylsuccinic	$C_7H_{12}O_4$	91°	Liquid
Isopropylsuccinic	$C_7H_{12}O_4$	114°	,,
symm. Methylethylsuccinic (fumaroid) .	$C_7H_{12}O_4$	180°	—
,, ,, (maleinoid) .	$C_7H_{12}O_4$	101°–102°	Liquid
asymm. ,, ...	$C_7H_{12}O_4$	104°	,,
Trimethylsuccinic	$C_7H_{12}O_4$	152°	38°
Butylsuccinic	$C_8H_{14}O_4$	81°	—
Isobutylsuccinic	$C_8H_{14}O_4$	109°	Liquid
symm. Methylpropylsuccinic (fumaroid) .	$C_8H_{14}O_4$	158°–160°	,,
,, ,, (maleinoid) .	$C_8H_{14}O_4$	92°–93°	,,
,, Methylisopropylsuccinic (fumaroid)	$C_8H_{14}O_4$	174°–175°	46°
,, ,, (maleinoid)	$C_8H_{14}O_4$	125°–126°	Liquid
,, Diethylsuccinic (fumaroid) . .	$C_8H_{14}O_4$	189°–190°	,,
,, ,, (maleinoid) . .	$C_8H_{14}O_4$	129°	,,
asymm. ,, ...	$C_8H_{14}O_4$	86°	,,
aa-Dimethyl-*a*-ethylsuccinic	$C_8H_{14}O_4$	139°–140°	,,
Tetramethylsuccinic . . . : .	$C_8H_{14}O_4$	200°	147°
Isoamylsuccinic	$C_9H_{16}O_4$	75°–76°	—
n-Hexylsuccinic	$C_{10}H_{18}O_4$	87°	57°
symm. Dipropylsuccinic (fumaroid) . :	$C_{10}H_{18}O_4$	182°–183°	Liquid
,, ,, (maleinoid) . .	$C_{10}H_{18}O_4$	119°–121°	,,
n-Heptylsuccinic	$C_{11}H_{20}O_4$	90°–91°	—
symm. Diisobutylsuccinic (fumaroid) .	$C_{12}H_{22}O_4$	195°	Liquid
,, ,, (maleinoid) .	$C_{12}H_{22}O_4$	97°–98°	,,
Tetraethylsuccinic	$C_{12}H_{22}O_4$	149°	86°
Tetrapropylsuccinic	$C_{16}H_{30}O_4$	137°	—

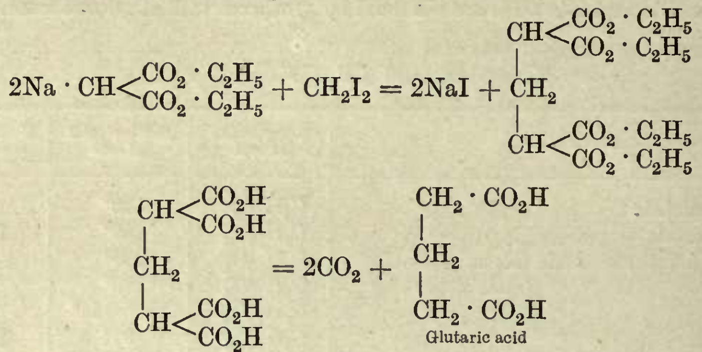
Pure succinic acid crystallises in monoclinic plates, m.-pt. 182°, b.-pt. 235°, having a disagreeable acid taste. When subjected to distillation, it loses water and yields *succinic anhydride*. Its solubility in water is 1 : 20 at the ordinary temperature, and it is highly resistant to the action of oxidising agents.

Calcium succinate is soluble in water; *ferric succinate* is used in the estimation of iron.

(*b*) ISOSUCCINIC ACID (Ethylidenesuccinic or Methylpropandioic Acid), $CH_3\cdot CH<^{CO_2H}_{CO_2H}$, forms needles or prisms which melt at 130° with evolution of CO_2 and formation of propionic acid. It is more soluble in water than its isomeride, but yields no anhydride. It is obtained by synthesis from ethyl malonate, or by treatment of *a*-bromopropionic acid with KCN and subsequent hydrolysis.

PYROTARTARIC ACIDS, $C_5H_8O_4$ (Four Isomerides)

(*a*) **GLUTARIC ACID** (Normal Pyrotartaric or Pentadioic Acid), $CO_2H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, forms crystals melting at 97·5° and is readily soluble in water. It is obtained from 1 mol. of methylene iodide and 2 mols. of ethyl sodiomalonate, the intermediate product being hydrolysed and 2 mols. of CO_2 then eliminated by heating :

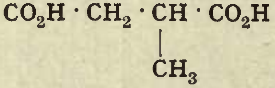


$$2\mathrm{Na}\cdot\mathrm{CH}{<}\begin{matrix}\mathrm{CO_2\cdot C_2H_5}\\ \mathrm{CO_2\cdot C_2H_5}\end{matrix} + \mathrm{CH_2I_2} = 2\mathrm{NaI} + \begin{array}{l}\mathrm{CH}{<}\begin{matrix}\mathrm{CO_2\cdot C_2H_5}\\ \mathrm{CO_2\cdot C_2H_5}\end{matrix}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH}{<}\begin{matrix}\mathrm{CO_2\cdot C_2H_5}\\ \mathrm{CO_2\cdot C_2H_5}\end{matrix}\end{array}$$

$$\begin{array}{l}\mathrm{CH}{<}\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH}{<}\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\end{array} = 2\mathrm{CO_2} + \begin{array}{l}\mathrm{CH_2\cdot CO_2H}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{array}$$

Glutaric acid

(*b*) **PYROTARTARIC ACID** (Methylbutandioic Acid),



$$\begin{array}{c}\mathrm{CO_2H\cdot CH_2\cdot CH\cdot CO_2H}\\ \quad\quad\; |\\ \quad\quad\;\mathrm{CH_3}\end{array}$$

is formed, together with pyruvic acid, when ordinary tartaric acid is subjected to dry distillation; synthetically it is prepared from ethyl acetoacetate. It forms small triclinic crystals melting at 117° and its anhydride is known. Since it contains an asymmetric carbon atom, it exists in two optically active stereoisomerides.

HIGHER HOMOLOGUES

The dialkylsuccinic acids (*see above*) contain two asymmetric carbon atoms and give rise to important cases of stereoisomerism. Together with the homologues of glutaric and adipic acids, they are found among the products of decomposition of the *terpenes* and hence serve to establish the composition of these.

β-METHYLADIPIC ACID, $CO_2H \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CO_2H$, melts at 85° and occurs along with menthol, etc., in the oxidation products of numerous ethereal oils.

SUBERIC ACID (Octandioic Acid), $CO_2H \cdot [CH_2]_6 \cdot CO_2H$, is obtained by boiling cork waste or fatty oils with nitric acid; it melts at 141° and its anhydride at 62°, while its *ethyl ester* boils at 281°. Distillation of the calcium salt yields *suberone* (*ketoheptamethylene*).

AZELAIC ACID, $CO_2H \cdot [CH_2]_7 \cdot CO_2H$, is now obtained easily and cheaply by decomposing the ozonides of oils and of the corresponding unsaturated fatty acids, especially of oleic acid (E. Molinari, Soncini, and Fenaroli, 1906–1908). The acid originally cost £24 per kilo, but can now be sold for a few shillings. It is obtained well crystallised from benzene or from water, in which it dissolves easily in the hot but only slightly in the cold (1·648 per cent. at 55°, 0·817 per cent. at 44·5°, 0·214 per cent. at 22°, and 0·212 per cent. at 15°); it is soluble also in alcohol or ether, melts at 106°, and gives a calcium salt which dissolves in cold but not in hot water.

SEBACIC ACID (Decandioic Acid), $CO_2H \cdot [CH_2]_8 \cdot CO_2H$, melts at 133° and is formed when oleic acid is dry-distilled or when stearic or ricinoleic acid is oxidised with nitric acid. Its anhydride melts at 78° and its diethyl ester boils at 196°.

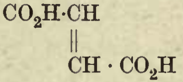
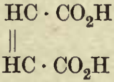
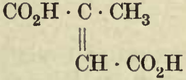
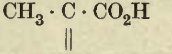
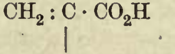
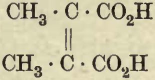
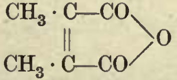
Sebacic acid is now used industrially for the separation of thorium from the rare earths (*see* Vol. I., p. 505).

HIGHER HOMOLOGUES OF OLEFINEDICARBOXYLIC ACIDS

Name of Acid	Structure $X = CO_2H$	Melting-point of acid	Melting-point of the anhydride	Boiling-point of the anhydride
Dimethylfumaric (α-methylmesaconic)	$CH_3 \cdot CX : CX \cdot CH_3$	239°–240°	—	—
Ethylfumaric (γ-methylmesaconic)	$CH_3 \cdot CH_2 \cdot CX : CHX$	194°–196°	—	—
Ethylmaleic (γ-methylcitraconic)	$CH_3 \cdot CH_2 \cdot CX : CHX$	100°	Liquid	229°
α-Methylitaconic	$CH_2 : CX \cdot CHX \cdot CH_3$	150°–151°	62°–63°	—
γ-Methylitaconic	$CH_3 \cdot CH : CX \cdot CH_2X$	166°–167°	—	—
Propylfumaric	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CX : CHX$	174°–175°	—	—
Propylmaleic	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CX : CHX$	93°–95°	—	243°–245°
γ-Ethylitaconic	$CH_3 \cdot CH_2 \cdot CH : CX \cdot CH_2X$	162°–167°	—	—
Allylsuccinic	$CH_2 : CH \cdot CH_2 \cdot CHX \cdot CH_2X$	92°–93°	Liquid	About 20°
Isopropylfumaric	$(CH_3)_2CH \cdot CX : CHX$	185°–186°	—	—
Isopropylmaleic	$(CH_3)_2CH \cdot CX : CHX$	91°–93°	+ 5°	138° (61 mm)
γγ-Dimethylitaconic (teraconic)	$(CH_3)_2C : CX \cdot CH_2X$	160°–161°	44°	197° (22 mm.)
γ-Methylene-γ-methylpyrotartaric	$CH_2 : C(CH_3) \cdot CHX \cdot CH_2X$	146°–147°	Liquid	—
Methylethylmaleic	$CH_3 \cdot CH_2 \cdot CX : CX \cdot CH_3$	—	,,	230°
α-Ethylitaconic	$CH_2 : CX \cdot CHX \cdot CH_2 \cdot CH_3$	150°	52°	—
αγ-Dimethylitaconic	$CH_3 \cdot CH : CX \cdot CHX \cdot CH_3$	202°	Liquid	131° (16 mm.)
αα-Dimethylitaconic	$CH_2 : CX \cdot CX(CH_3)_2$	142·5°	,,	210°–215°
Butylfumaric	$C_2H_5 \cdot CH_2 \cdot CH_2 \cdot CX : CHX$	170°	—	—
Butylmaleic	$C_2H_5 \cdot CH_2 \cdot CH_2 \cdot CX : CHX$	80°	—	—
γ-Propylitaconic	$C_2H_5 \cdot CH_2 \cdot CH : CX \cdot CH_2X$	159°–160°	—	—
Isobutylfumaric	$(CH_3)_2CH \cdot CH_2 \cdot CX : CHX$	183°	—	—
Isobutylmaleic	$(CH_3)_2CH \cdot CH_2 \cdot CX : CHX$	78°–81°	—	—
γ-Isopropylitaconic	$(CH_3)_2CH \cdot CH : CX \cdot CH_2X$	189°–192°	—	—
Methylpropylmaleic	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CX : CX \cdot CH_3$	—	Liquid	241°–242°
Methylisopropylmaleic	$(CH_3)_2CH \cdot CX : CX \cdot CH_3$	—	,,	240°–242°
Diethylmaleic	$C_2H_5 \cdot CX : CX \cdot C_2H_5$	—	,,	239°–240°
γ-Methyl-α-ethylitaconic	$CH_3 \cdot CH : CX \cdot CHX \cdot C_2H_5$	136°	,,	143° (12 mm.)

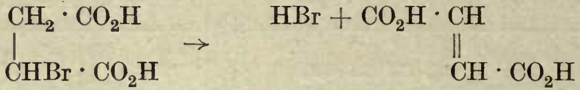
B. UNSATURATED DIBASIC ACIDS

I. OLEFINEDICARBOXYLIC ACIDS, $C_nH_{2n-4}O_4$

$C_4H_4O_4$	Fumaric acid	 $\begin{array}{c} CO_2H \cdot CH \\ \Vert \\ CH \cdot CO_2H \end{array}$	melts at 200°	(sublimes)
,,	Maleic acid	 $\begin{array}{c} HC \cdot CO_2H \\ \Vert \\ HC \cdot CO_2H \end{array}$	,, 130°	boils at 160°
$C_5H_6O_4$	Mesaconic acid	 $\begin{array}{c} CO_2H \cdot C \cdot CH_3 \\ \Vert \\ CH \cdot CO_2H \end{array}$	,, 202°	—
,,	Citraconic acid	 $\begin{array}{c} CH_3 \cdot C \cdot CO_2H \\ \Vert \\ CH \cdot CO_2H \end{array}$	,, 91°	—
,,	Itaconic acid	 $\begin{array}{c} CH_2 : C \cdot CO_2H \\ \vert \\ CH_2 \cdot CO_2H \end{array}$	,, 161°	—
,,	Glutaconic acid	$CO_2H \cdot CH : CH \cdot CH_2 \cdot CO_2H$	,, 132°	—
$C_6H_8O_4$	Pyrocinchonic acid	 $\begin{array}{c} CH_3 \cdot C \cdot CO_2H \\ \Vert \\ CH_3 \cdot C \cdot CO_2H \end{array}$	—	—
$C_6H_6O_3$	Pyrocinchonic anhydride		,, 96°	boils at 223°
$C_6H_8O_4$	αβ-Hydromucic acid	$CO_2H \cdot CH_2 \cdot CH_2 \cdot CH : CH \cdot CO_2H$	,, 169°	(stable)
	βγ- ,, ,,	$CO_2H \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO_2H$	,, 195°	(labile)

As far as the carboxyl groups are concerned, these acids have chemical properties similar to those of the saturated dibasic acids (*see* p. 364), whilst, as they are unsaturated compounds, they are able to combine with 2 atoms of hydrogen or halogen or with 1 mol. of a halogen hydracid.

They are usually prepared from the mono- and di-halogen substitution products of succinic acid and its homologues by removing either 1 mol. of halogen hydracid (by heating with KOH) or 2 atoms of halogen:

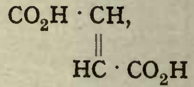


$$\begin{array}{lcl} CH_2\cdot CO_2H & & HBr + CO_2H\cdot CH \\ | & \rightarrow & \qquad\qquad\quad \| \\ CHBr\cdot CO_2H & & \qquad\qquad\quad CH\cdot CO_2H \end{array}$$

Monobromosuccinic acid Fumaric acid

Distillation of the saturated dibasic hydroxy-acids results in the removal of 1 mol. of H_2O and the formation of unsaturated acids.

The most interesting cases of stereoisomerism were considered on p. 21. When fumaric acid is either heated or treated with PCl_5, $POCl_3$, or P_2O_5, it is converted into maleic anhydride. Maleic acid is transformed into fumaric acid by heating at 200° in a sealed tube or by the action of bromine or of various acids in presence of sunlight.

FUMARIC ACID (trans-Butendioic Acid), $C_4H_4O_4$ or 

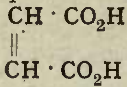
$$\begin{array}{l} CO_2H\cdot CH, \\ \qquad\quad \| \\ \qquad HC\cdot CO_2H \end{array}$$

forms small white prisms which have a marked acid taste and are almost insoluble in water; it does not melt, but sublimes at about 200°, subsequently losing water and becoming converted largely into maleic anhydride.

It is moderately widespread in certain vegetable organisms, *e. g.*, in fungi, truffles, Iceland moss, and especially in *Fumaria officinalis*. It may be prepared by the ordinary synthetical methods and also by the action of phosphorus and bromine on succinic acid, the product obtained being decomposed by heating with water.

It is stereoisomeric with maleic acid (*see* p. 22) and its reduction to normal succinic acid by means of nascent hydrogen confirms its constitution, which is also deduced from the decomposition of the corresponding ozonide (Harries).

The Silver Salt, $C_4H_2O_4Ag_2$, is slightly soluble in water, and the same is the case with the barium salt, $C_4H_2O_4\ Ba + 3H_2O$, which in boiling water becomes insoluble and separates in the anhydrous form, $C_4H_2O_4Ba$.

MALEIC ACID (cis-Butendioic Acid), $C_4H_4O_4$ or 

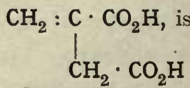
$$\begin{array}{l} CH\cdot CO_2H, \\ \| \\ CH\cdot CO_2H \end{array}$$

forms large prisms melting at 130° and having an unpleasant taste; it boils at 160°, losing water and becoming converted partially into maleic anhydride. It is readily soluble in water.

Its ready transformation into maleic anhydride is explained by the stereochemical relations considered on pp. 21 *et seq.*, and in many general methods of preparing the acid, the anhydride is first obtained.

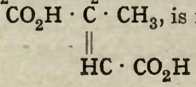
The Barium Salt, $C_4H_2O_4Ba + H_2O$, is soluble in hot water, from which it crystallises well.

Electrolysis of the alkali salts of fumaric and maleic acids yields acetylene. When heated with sodium hydroxide at 100°, these two acids are converted into inactive malic acid.

ITACONIC ACID (Methylenesuccinic Acid), $C_5H_6O_4$ or 

$$\begin{array}{l} CH_2 : C\cdot CO_2H, \\ \qquad\quad | \\ \qquad\quad CH_2\cdot CO_2H \end{array}$$

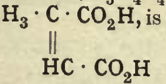
is a white substance melting at 161° and non-volatile in steam. It is obtained by the action of water on its anhydride, the latter being formed by the interaction of citraconic anhydride and water at 150°. Hydrogen converts it into pyrotartaric acid and permanganate into hydroxyparaconic acid. On electrolysis it yields *allene*, $CH_2 : C : CH_2$.

MESACONIC ACID (Methylfumaric Acid), $C_5H_6O_4$ or 

$$\begin{array}{l} CO_2H\cdot C\cdot CH_3, \\ \qquad\quad \| \\ \qquad\quad HC\cdot CO_2H \end{array}$$

is formed by

heating citraconic or itaconic acid with water at 200° or by treatment of citraconic acid with dilute HNO_3 or concentrated NaOH, or with traces of bromine in sunlight. It is difficultly soluble in water, melts at 202°, and does not distil in steam. When electrolysed it forms *allylene*, $CH_3 \cdot C \vdots CH$, while with hydrogen it gives pyrotartaric acid and with permanganate, pyrotartaric and oxalic acids. It forms a barium salt, $C_5H_4O_4Ba + 4H_2O$.

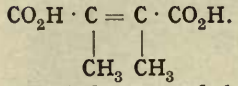
CITRACONIC ACID (**Methylmaleic Acid**), $C_5H_6O_4$ or  $\begin{array}{l} CH_3 \cdot C \cdot CO_2H \\ \quad \| \\ HC \cdot CO_2H \end{array}$, is formed from the corresponding anhydride and water. It melts at 91°, differs from the two preceding acids by being very soluble in water, distils in steam and readily gives the anhydride again. On electrolysis it yields *allylene*, while with hydrogen it forms pyrotartaric acid.

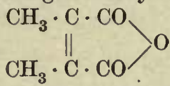
GLUTACONIC ACID, $C_5H_6O_4$ or $CO_2H \cdot CH : CH \cdot CH_2 \cdot CO_2H$, is isomeric with the three preceding acids, and is obtained by hydrolysing the corresponding ester with HCl; it melts at 132° and the hydrogen of its CH_2-group is replaceable by sodium (*see* p. 368).

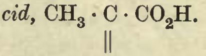
Of the higher homologues of these acids mention may be made of the *alkylitaconic acids*, with which, on heating with NaOH solution, the position of the double linking changes, gives alkylmesaconic and *alkylaticonic acids* (Fittig), *e. g.*, *isobutylaticonic acid*, $(CH_3)_2CH \cdot CH : CH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, which melts at 93°; with alkalis these acids undergo the reverse change to some extent.

The calcium and barium salts of the alkylmesaconic acids are readily soluble in water, and those of the alkylitaconic acids slightly soluble.

Of these homologous acids, the following deserve mention:

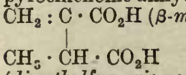
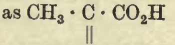
PYROCINCHONIC ACID (**Dimethylmaleic** or **Dimethylfumaric Acid**), $C_6H_8O_4$ or  $\begin{array}{l} CO_2H \cdot C = C \cdot CO_2H \\ \qquad\ \ | \quad\ \ | \\ \qquad CH_3\ CH_3 \end{array}$. Of the two stereoisomerides, only dimethylmaleic acid was until recently known, and then only as the anhydride, namely, *pyrocinchonic anhydride* (m.-pt. 96°, b.-pt. 223°). Dimethylmaleic acid cannot exist in the free state, as it immediately gives up water, forming the anhydride; its esters are, however, known.

The anhydride,  $\begin{array}{l} CH_3 \cdot C \cdot CO \\ \quad\ \| \qquad\quad > O \\ CH_3 \cdot C \cdot CO \end{array}$, may be prepared in various ways, *e. g.*, by distilling in steam the product of the interaction of pyrotartaric acid and sodium succinate, but a better yield is obtained by first preparing the nitrile of methylacetoacetic acid and distilling this in a vacuum.

According to A. Bischoff, the stereoisomeride, *Dimethylfumaric Acid*,  $\begin{array}{r} CH_3 \cdot C \cdot CO_2H \\ \| \quad\quad \\ CO_2H \cdot C \cdot CH_3 \end{array}$, could not, owing to stereochemical considerations, be formed in the free state, but Fittig and Kettner (1899) and also E. Molinari (1900) have succeeded in isolating it in various ways.[1] It forms white crystals, m.-pt. 152°; its amido-derivatives have also been prepared.

Bauer (1904) made the interesting observation that dimethylfumaric acid and, in general, compounds containing carboxyl or alkyl or phenyl groups or bromine atoms united to two carbon atoms connected by a double linking, *do not unite with bromine.*

---

[1] Fittig and Kettner, making use of the property of *various acids, homologous with citraconic acid, of yielding the corresponding fumaroid isomeride when simply heated with alkali*, obtained from pyrocinchonic anhydride the two acids: one melting at 151°, to which is ascribed the constitution  $\begin{array}{l} CH_2 : C \cdot CO_2H \\ \qquad\ | \\ CH_3 \cdot CH \cdot CO_2H \end{array}$ (*β-methylitaconic acid*), and another melting at 240° and regarded as  $\begin{array}{r} CH_3 \cdot C \cdot CO_2H \\ \| \quad\quad \\ CO_2H \cdot C \cdot CH_3 \end{array}$ (*dimethylfumaric acid*). It is highly probable, for the following reasons, that the latter constitution should be attributed to the acid melting at 151°:

By a long series of investigations (1881 to 1896), Körner and Menozzi showed that, in general, *the treatment of α-amino-acids with methyl iodide in presence of caustic potash yields the corresponding betaines* (condensed alkyl-substituted amines), *but the β-amino-acids, if similarly treated, always yield the corresponding unsaturated, non-nitrogenous acids of the fumaroid type* (betaines being probably formed as intermediate products). *As the same β-amino-acid can be obtained from the two stereoisomeric unsaturated acids, this general reaction renders it possible to pass from a maleinoid unsaturated acid to the corresponding fumaroid stereoisomeride.* By applying this reaction to pyrocinchonic anhydride, E. Molinari arrived at the expected stereoisomeride (*dimethylfumaric acid*), melting at 152°.

HYDROMUCONIC ACIDS, $C_6H_8O_4$. Of these are known (1) the αβ-unsaturated acid, $CO_2H \cdot \underset{\delta}{CH_2} \cdot \underset{\gamma}{CH_2} \cdot \underset{\beta}{CH} : \underset{\alpha}{CH} \cdot CO_2H$, which is *stable* and melts at 169°; with permanganate it yields succinic acid. (2) The *unstable* βγ-acid, $CO_2H \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO_2H$, which melts at 195° and is obtained by reducing muconic acid; when heated with alkali, it is converted into the stable isomeride, whilst with permanganate it gives malonic acid, $CO_2H \cdot CH_2 \cdot CO_2H$.

Of the **DIOLEFINEDICARBOXYLIC ACIDS**, only **Muconic Acid**, $CO_2H \cdot CH : CH \cdot CH : CH \cdot CO_2H$, melting above 260°, need be referred to.

Of the **ACETYLENEDICARBOXYLIC ACIDS**, mention will be made only of **Acetylenedicarboxylic (Butindioic) Acid**, $CO_2H \cdot C \equiv C \cdot CO_2H$, which melts and decomposes at 175°; it crystallises with $2H_2O$. It is obtained on removing HBr from dibromo- or isodibromo-succinic acid by means of potash.

Diacetylenedicarboxylic Acid, $CO_2H \cdot C \equiv C \cdot C \equiv C \cdot CO_2H + H_2O$, turns dark red in the light and explodes at 177°. When reduced with sodium amalgam, it yields hydromuconic acid.

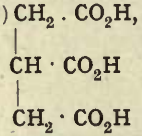
Tetracetylenedicarboxylic Acid, $CO_2H \cdot C \equiv C \cdot C \equiv C \cdot C \equiv C \cdot C \equiv C \cdot CO_2H$, forms white crystals which blacken rapidly in the light and explode violently on heating.

C. TRIBASIC ACIDS

These have usually been obtained synthetically, and are not very stable, since they readily yield carbon dioxide and dibasic acids when heated; their esters, however, exhibit increased stability. Their properties and methods of preparation vary according as the carboxyl groups are united to one or to various carbon atoms.

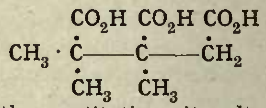
Of the many such acids known, the following may be mentioned:

TRICARBALLYLIC ACID (symm. ωαω′-**Propanetricarboxylic** or **Pentanedioic-3-methyloic Acid**) $CH_2 . CO_2H$, occurs in the deposits left on concentrating beet-sugar juices *in vacuo*. Synthetically it is obtained by converting glycerol into the tribromohydrin or allyl tribromide, which is treated with potassium cyanide to give the corresponding tricyano-compound, the latter being then hydrolysed to tricarballylic acid; the constitution of the acid is thus proved. This acid forms white, prismatic crystals melting at 166°. It may also be prepared by reducing unsaturated tricarboxylic acids (*e. g.*, aconitic acid).



$$\begin{array}{l} CH_2 \cdot CO_2H \\ | \\ CH \cdot CO_2H \\ | \\ CH_2 \cdot CO_2H \end{array}$$

CAMPHORONIC ACID (ααβ-**Trimethylcarballylic Acid**), is formed on oxidising camphor, of which it serves to indicate the constitution; it melts at 135°.



$$\begin{array}{lllll} & CO_2H & & CO_2H & CO_2H \\ CH_3 \cdot & C & — & C & — CH_2 \\ & CH_3 & & CH_3 & \end{array}$$

ACONITIC ACID is an unsaturated tribasic acid of the constitution $CO_2H \cdot CH_2 \cdot C(CO_2H) : CH \cdot CO_2H$, and is found in beetroot, sugar-cane, *Aconitum napellus*, etc. It is obtained synthetically by eliminating CO_2 from citric acid by the action of heat or of various reagents. It melts at 191°, losing CO_2, and forming itaconic anhydride. It dissolves readily in water and with nascent hydrogen generates tricarballylic acid, its structure being indicated by this reaction.

D. TETRABASIC ACIDS

These are formed from ethyl sodiomalonate (*see* p. 368) by means of an unsaturated ester, *e. g.*, of fumaric acid. When heated, they lose CO_2, forming tribasic and, better, dibasic acids.

Olefinetetracarboxylic Acids are also known.

FF. DERIVATIVES OF THE ACIDS

I. HALOGEN DERIVATIVES

One or more of the hydrogen atoms of an alkyl group united with carboxyl may be replaced by halogens, the carboxyl group being left intact. The *halogen derivatives of the acids*, thus obtained, are more markedly acid in character than the original substances. They are obtained by the action of chlorine or bromine in sunlight or, better, by heating the acid with the halogen in presence of a little water or sulphur.

On the other hand, the hydroxyl of the carboxyl group may be replaced, forming *acid halides :* — CO — X (by treating the acid with phosphorus chloride or bromide). That the halogen has replaced the hydroxyl group is shown by the fact that these acid halides yield the original acids when treated with cold water, whilst halogens are not displaced from alkyl residues in this way. These acid chlorides and bromides readily give the monochloro- and monobromo- acids when treated further with chlorine or bromine.

(*a*) HALOGENATED ACIDS

When the carbon atom (*a*), to which the carboxyl group is attached, is not united directly with hydrogen [*e. g.*, in trimethylacetic acid, $(CH_3)_3C \cdot CO_2H$], bromine is not taken up (*see* p. 375). The constitution of a halogenated acid, or rather the position of the halogen atom, is deduced from that of the corresponding *hydroxy-acid* (containing a hydroxyl group in place of the halogen) obtained by heating the halogenated acid with sodium carbonate solution or with water and lead oxide.

On the other hand, the passage from hydroxy-acid to the corresponding halogenated acid may be effected by treatment with phosphorus chloride or bromide.

The acid character becomes more marked on passing from the iodo- to the bromo- and then to the chloro-compounds, and also increases with the number of halogen atoms in the molecule.

While the α-halogenated acids readily yield the corresponding hydroxy-acids, the β-acids yield the corresponding unsaturated acids (*see* p. 352) and may even lose CO_2, giving unsaturated hydrocarbons, but the γ-halogenated acids, when heated with sodium carbonate solution or with water alone, give up a molecule of halogen hydracid and yield, not the unsaturated acids, but *lactones* (*see* p. 355).

When halogenated acids are prepared by the interaction of an unsaturated acid with a halogen hydracid (*e. g.*, HI), the halogen becomes attached to the least hydrogenated carbon atom (*see* p. 116). Thus, with a $\Delta^{\alpha\beta}$-acid, where the double linking is between the α- and β-carbon atoms, the halogen unites with the latter.

The halogenated and poly-halogenated acids exhibit isomerism, since the halogen atom may be joined to the α, β, γ, etc., carbon atom, or several halogen atoms may be united with one and the same carbon atom or with different ones.

When heated with potassium cyanide, the mono-haloid acids yield *cyano-acids :*

$$\underset{\text{Potassium chloroacetate}}{CH_2Cl \cdot COOK} + KCN = KCl + \underset{\text{Potassium cyanoacetate}}{CN \cdot CH_2 \cdot COOK}.$$

With sodium sulphite they give dibasic *sulpho-acids*, the sulphonic group of which is readily replaced by hydroxyl by boiling with alkali :

$$Na_2SO_3 + Cl \cdot CH_2 \cdot COONa = NaCl + \underset{\text{Sodium sulphoacetate}}{SO_3Na \cdot CH_2 \cdot COONa}$$

With reference to the affinities of the halogenated acids, *see* Note on p. 323.

HALOGEN DERIVATIVES OF THE SATURATED MONOBASIC ACIDS

Formula	Name	Melting-point	Boiling-point	Preparation and properties
$CHCl_2 \cdot CO_2H$	Dichloroacetic acid	—	191°	By heating: $CCl_3 \cdot CHO + KCN + H_2O = CHCl_2 \cdot CO_2H + KCl + HCN$ When heated with alkali, it gives oxalic and acetic acids. The silver salt with water gives *glyoxylic acid*, $CHO \cdot CO_2H$.
$CCl_3 \cdot CO_2H$	Trichloroacetic acid	55°	195°	By oxidising chloral with nitric acid. With alkali in the hot it gives chloroform and CO_2.
$CN \cdot CH_2 \cdot CO_2H$	Cyanoacetic acid	70°	—	Gives malonic acid on hydrolysis.
$CH_3 \cdot CHCl \cdot CO_2H$	α-Chloropropionic acid	—	186°	Lactic acid + $PCl_5 = CH_3 \cdot CHCl \cdot COCl$ (*lactyl chloride*), which with $H_2O = HCl + CH_3 \cdot CHCl \cdot CO_2H$.
$CH_2Cl \cdot CH_2 \cdot CO_2H$	β-Chloropropionic acid	41·5°	204°	Acroleïn + HCl = β-chloropropaldehyde, which with HNO_3 → β-chloropropionic acid.
$CH_3 \cdot CCl_2 \cdot CO_2H$	αα-Dichloropropionic acid	—	188°	From propionic acid + Cl (similarly for the bromo-derivative).
$CH_2Cl \cdot CHCl \cdot CO_2H$	αβ-Dichloropropionic acid	50°	210°	Acrylic acid + Cl (similarly for the bromo-derivative).
$CHBr_2 \cdot CH_2 \cdot CO_2H$	ββ-Dibromopropionic acid	71°	—	β-Bromoacrylic acid + HBr.
$CH_2I \cdot CH_2 \cdot CO_2H$	β-Iodopropionic acid	82°	—	From acrylic acid + HI or from glyceric acid + phosphorus iodide.
$CH_3 \cdot CH_2 \cdot CHCl \cdot CO_2H$	α-Chloro-n-butyric acid	—	158°	
$CH_3 \cdot CHCl \cdot CH_2 \cdot CO_2H$	β-Chloro-n-butyric acid	—	—	From allyl cyanide.
$CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CO_2H$	γ-Chloro-n-butyric acid	10°	—	

MONOCHLORACETIC ACID (Chlorethanoic Acid), $CH_2Cl \cdot COOH$, is prepared by the general method, that is, by passing dry chlorine into hot acetic acid in presence of acetic anhydride, phosphorus, or sulphur (with 1 per cent. of sulphur, an 80 per cent. yield is obtained). It forms rhombic crystals which corrode the flesh and melt at 62°; on solidification an unstable modification is obtained which, for some time, melts at 52°; it boils at 186°. When heated with water or alkali it gives Hydroxyacetic Acid (*glycollic acid*), $OH \cdot CH_2 \cdot CO_2H$; with ammonia it yields Aminoacetic Acid (*glycine* or *glycocoll*), $NH_2 \cdot CH_2 \cdot CO_2H$.

The properties of the other halogenated acids are given in the Table on the preceding page.

(*b*) ACID HALIDES

Of these compounds the most important are the *chlorides* of the acid radicals, which are termed *acichlorides* or *chloranhydrides*. Although acetyl chloride, $CH_3 \cdot CO \cdot Cl$, is readily obtainable, it has not been found possible to prepare *formyl chloride*, $H \cdot CO \cdot Cl$, a mixture of $CO + HCl$ being always obtained.

These compounds are usually colourless liquids, which have pungent odours and fume strongly in the air, the moisture in the latter liberating hydrogen chloride. Their boiling-points are below those of the corresponding acids, and they distil without decomposing; the higher members are, however, solid and do not distil unchanged even in a vacuum.

The principal methods for preparing these substances are as follows:

(*a*) The organic acid is heated for a short time on the water-bath with PCl_5 (with higher acids), PCl_3 (with acids below C_{10}) or, in some cases, sulphuryl chloride, SO_2Cl_2:

$$\underset{\text{Lauric acid}}{C_{11}H_{23} \cdot CO \cdot OH} + PCl_5 = C_{11}H_{23} \cdot CO \cdot Cl + HCl + POCl_3,$$

the phosphorus oxychloride and hydrochloric acid being eliminated by distillation *in vacuo*; or,

$$3CH_3 \cdot CO \cdot OH + 2PCl_3 = 3CH_3 \cdot CO \cdot Cl + 3HCl + P_2O_3,$$

the acetyl chloride thus formed being separated by distillation, while the P_2O_3 is left in the residue.

(*b*) With thionyl chloride the acids yield the chloranhydrides, the other products formed at the same time being volatile and hence easily removable: $X \cdot CO \cdot OH + SOCl_2 = X \cdot CO \cdot Cl + HCl + SO_2$.

(*c*) In some cases the acid is treated simply with HCl in presence of a dehydrating agent, (P_2O_5): $CH_3 \cdot CO \cdot OH + HCl = H_2O + CH_3 \cdot CO \cdot Cl$.

CHEMICAL PROPERTIES. The great reactivity of the chlorine atom of these substances renders them of considerable importance in chemical syntheses. Water, ammonia (amines), and alcohols decompose them in the cold with great violence:

$$CH_3 \cdot CO \cdot Cl + H_2O = HCl + CH_3 \cdot CO \cdot OH$$
$$CH_3 \cdot CO \cdot Cl + NH_3 = HCl + CH_3 \cdot CO \cdot NH_2 \text{ (acetamide)}$$
$$CH_3 \cdot CO \cdot Cl + C_2H_5 \cdot OH = HCl + CH_3 \cdot CO \cdot OC_2H_5 \text{ (ethyl acetate).}$$

With organic salts they yield anhydrides:

$$CH_3 \cdot CO \cdot Cl + CH_3 \cdot CO \cdot ONa = NaCl + CH_3 \cdot CO \cdot O \cdot CO \cdot CH_3.$$

Sodium amalgam reduces them to aldehydes and then to alcohols.

ACETYL CHLORIDE (Ethanoyl Chloride), $CH_3 \cdot CO \cdot Cl$, is a liquid boiling at 51° and having the sp. gr. 1·105 at 20°. It is prepared by mixing 5 parts of glacial acetic acid and 4 parts of phosphorus trichloride in the cold, heating for a short time at 40° and, after evolution of HCl ceases, distilling the acetyl chloride and purifying it by rectification. Water decomposes it with development of heat.

It is employed in organic synthesis, since it readily yields acetyl derivatives of alcohols and of primary and secondary amines.

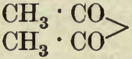
The commercial product costs 3*s.* to 4*s.* per kilo, and the chemically pure 14*s.*

The boiling-points of the higher homologues of acetyl chloride rise with the molecular weight and, with isomerides, that with the normal constitution has the highest boiling-point; the specific gravity diminishes as the molecular weight increases.

Acetyl iodide boils at 108°, *propionyl chloride* at 108° (the bromide at 104° and the iodide at 127°); *normal butyryl chloride* boils at 101° (the bromide at 128° and the iodide at 146°) and *isobutyryl chloride* at 92° (the bromide at 116°); *isovaleryl chloride* boils at 114° (the bromide at 143° and the iodide at 168°) and *trimethylacetyl chloride*, $(CH_3)_3C\cdot CO\cdot Cl$, at 105°.

II. ANHYDRIDES

The anhydrides of organic acids were discovered by C. Gerhardt in 1851 and correspond with those of the inorganic acids, that is, they may be regarded as products of the condensation of 2 mols. of acid with expulsion of 1 mol. of water. Here also, the organic anhydrides, when they are at all soluble, take up water and regenerate the acids. With organic acids, however, more varied and interesting cases are presented, since 2 mols. of different acids may condense (*mixed anhydrides*), while *internal anhydrides* may be formed by condensation between the two carboxyl groups of a dibasic acid.

The anhydrides may be regarded also as oxides of acid radicals, *e. g.*, acetic anhydride,  $\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\!>\!O$, or *acetyl oxide*, $(CH_3\cdot CO)_2O$.

PROPERTIES. The first members of the series are liquid, the higher ones solid; they generally dissolve but slightly in water, their transformation into acids being very slow. They have a neutral reaction and are soluble in ether and often in alcohol.

With ammonia and the primary and secondary amines, they form *amides* and ammoniacal salts: $(CH_3CO)_2O + 2NH_3 = CH_3\cdot CO\cdot NH_2$ (acetamide) $+ CH_3\cdot CO\cdot ONH_4$ (ammonium acetate).

When heated with an alcohol, they give the corresponding ester and acid:

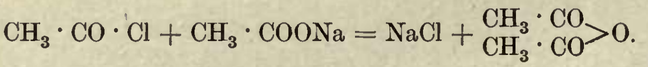
$$(CH_3CO)_2O + C_2H_5\cdot OH = CH_3\cdot COOC_2H_5 + CH_3\cdot COOH.$$

With halogen hydracids in the hot they yield the halides of the acids and the free acids: $(CH_3CO)_2O + HCl = CH_3\cdot CO\cdot Cl + CH_3\cdot COOH$.

With the halogens they give acid halides and halogenated acids: $(CH_3CO)_2O + Cl_2 = CH_3\cdot CO\cdot Cl + CH_2Cl\cdot CO_2H$.

Aldehydes combine with anhydrides, forming esters, while sodium amalgam reduces anhydrides to aldehydes and alcohols.

GENERAL METHODS OF PREPARATION. (*a*) By the action of acid chlorides on the dry alkali salts of the corresponding acids:



$$CH_3\cdot CO\cdot Cl + CH_3\cdot COONa = NaCl + \begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\!>\!O.$$

(*b*) The same result is obtained by the action of phosphorus oxychloride (or phosgene, $COCl_2$) on a mixture of the alkali and alkaline-earth salts of the corresponding acid, the acid chloride being formed as an intermediate product.

(*c*) The higher anhydrides are obtained from the corresponding acids by the action of acetyl chloride:

$$CH_3\cdot COCl + 2X\cdot COOH = HCl + CH_3\cdot COOH + (X\cdot CO)_2O.$$

(*d*) The formation of anhydrides from the acids by the subtraction of water (by means of P_2O_5) gives low yields, the best being obtained with palmitic and stearic acids (using acetic anhydride in the hot as dehydrating agent).

The properties of the best-known anhydrides are given in the following Table:

Formula	Name	Melting-point	Boiling-point	Specific gravity
$(CH_3 \cdot CO)_2O$	Acetic anhydride	—	136·5°	1·078 (at 21°)
$(C_2H_5 \cdot CO)_2O$	Propionic anhydride	—	168·6°	1·034 (at 0°)
$(C_3H_7 \cdot CO)_2O$	norm. Butyric anhydride	—	192°	0·978 (at 12·5°)
,,	Isobutyric anhydride	—	182°	0·958 (at 16·5°)
$(C_4H_9 \cdot CO)_2O$	Isovaleric anhydride	—	215°	—
,,	Trimethylacetic anhydride	—	190°	—
$(C_5H_{11} \cdot CO)_2O$	norm. Caproic anhydride	—	242°	0·928 (at 17°)
$C_6H_{13} \cdot CO)_2O$	Œnanthic anhydride	+ 17°	257°	0·912 (at 17°)
$(C_7H_{15} \cdot CO)_2O$	Caprylic anhydride	− 1°	186° (15 mm.)	—
$(C_8H_{17} \cdot CO)_2O$	Pelargonic anhydride	+ 16°	207° ,,	—
$(C_{11}H_{23} \cdot CO)_2O$	Lauric anhydride	+ 41°	166° (vacuum)	—
$(C_{13}H_{27} \cdot CO)_2O$	Myristic anhydride	+ 51°	198° ,,	—
$(C_{15}H_{31} \cdot CO)_2O$	Palmitic anhydride	55°–66°	—	—
$(C_{17}H_{35} \cdot CO)_2O$	Stearic anhydride	72°	—	—

ACETIC ANHYDRIDE (Ethanoic Anhydride), $(CH_3 \cdot CO)_2O$, is of importance industrially owing to its use in many organic syntheses, as it readily gives acetyl derivatives with alcohols or with primary or secondary amines. It is a suitable reagent for determining how many hydroxyl groups an organic substance contains (*see* Acetyl Number, p. 224).

The largest industrial consumption of acetic anhydride is for making *acetylcellulose* used for non-inflammable cinematograph films and for aeroplane dope; its use for artificial silk is also anticipated (*see:* Textile fibres). Large quantities of the anhydride are likewise employed in making organic dyes, perfumes and drugs.

It is a colourless, very mobile liquid, b.-pt. 139·5°, sp. gr. 1·078 at 21° and 1·0876 at 15°, index of refraction 1·39069 at 15°; it has a pungent odour.

It dissolves without alteration in 10 parts of cold water and is converted into acetic acid only when heated, the last portions only on prolonged boiling.[1]

It is prepared by dropping 5 parts of acetyl chloride on to 7 parts of dry powdered sodium acetate, which is kept cool meanwhile. The mixture is subsequently gently heated for a short time and the anhydride then distilled off on a sand-bath.

The commonest method of preparing it industrially appears to be that utilising the

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[1] Since commercial acetic anhydride often contains considerable proportions of acetic acid (10 to 25 per cent.), determination of its strength by titration requires the following precautions: A weighed quantity (about 0·5 gram) of the anhydride is introduced into a flask containing 100 c.c. of clear baryta water of known titre (corresponding, for example, with 94 c.c. of $\frac{N}{10}$ — HCl), the liquid being then boiled for about half an hour under a reflux condenser fitted with a soda-lime tube to prevent access of CO_2. It is then allowed to cool somewhat, the excess of baryta being rapidly titrated with decinormal hydrochloric acid in presence of a drop of phenolphthalein. Another method of hydrolysing the acetic anhydride consists in boiling it as above for forty-five minutes with at least 100 times its weight of freshly-boiled water (free from CO_2); the cold liquid is then titrated with decinormal caustic soda in presence of phenolphthalein. The acidity is calculated as though it were all due to acetic acid, the excess of the resulting percentage over 100 being multiplied by 5·67 to give the percentage of acetic anhydride in the sample analysed; subtraction of this number from 100 gives the percentage of acetic acid present. Thus, if the titration indicates 115·86 per cent. of acetic acid, the percentage of acetic anhydride will be 15·86 × 5·67 = 89·92 and that of acetic acid, 100 − 89·92 = 10·08.

Sulphurous anhydride present (rarely) as impurity is determined by means of iodine solution, sulphuric acid by barium chloride, and hydrochloric acid by decinormal silver nitrate solution with potassium chromate as indicator.

reaction between sodium acetate and sulphuryl chloride [1] (*see* Vol. I., p. 330), which occurs in two phases:

$$2CH_3 \cdot CO_2Na + SO_2Cl_2 = Na_2SO_4 + 2CH_3 \cdot CO \cdot Cl$$
$$CH_3 \cdot CO \cdot Cl + CH_3 \cdot CO_2Na = NaCl + (C_2H_3O)_2O.$$

In practice rather more than the theoretical quantity of sodium acetate is used, and all the operations are carried out in closed vessels to prevent access of moisture and loss of sulphuryl chloride with its unpleasant odour. The sodium acetate should previously be dried at 140° to reduce the moisture content to 0·1 per cent., and the sulphuryl chloride used should distil to the extent of 92 per cent. between 68° and 69·5° and should have the sp. gr. 1·675. Fig. 253 represents a scheme for an acetic anhydride works: The sodium acetate is subjected to preliminary heating in 1 and is then dried completely in three vacuum vessels below (2*d*, 2*b*, 2*c*), the suction pump being at 10. The perfectly dry salt is distributed in several apparatus fitted with stirrers on the ground-floor (3*a*–3*g*), the sulphuryl chloride being introduced from the tank 4 and measured in 4*a*–4*g*. In order that the temperature may not rise much, the sulphuryl chloride is fed gradually into each vessel, which is fitted with a small reflux condensing column. When the reaction is finished the different apparatus act as stills and are put into communication with the vacuum pump 10 through the collecting vessels 6*a*–6*g* and the condensers for the crude acetic anhydride, 5*a*–5*g*; 7 is the general collecting tank for the crude product, which contains about 90 per cent. of the anhydride, the remainder being acetic acid, acetyl chloride, sulphur dioxide and other secondary products. The anhydride is purified by distillation in a vacuum over anhydrous sodium acetate, followed by vacuum rectification (by means of pump 11) in a continuous column apparatus, 9–9*d*; 0·3–1 per cent. of fuming nitric acid (U.S. Pat. 1,069,168, 1913) or ozonised air may be used in the purification.

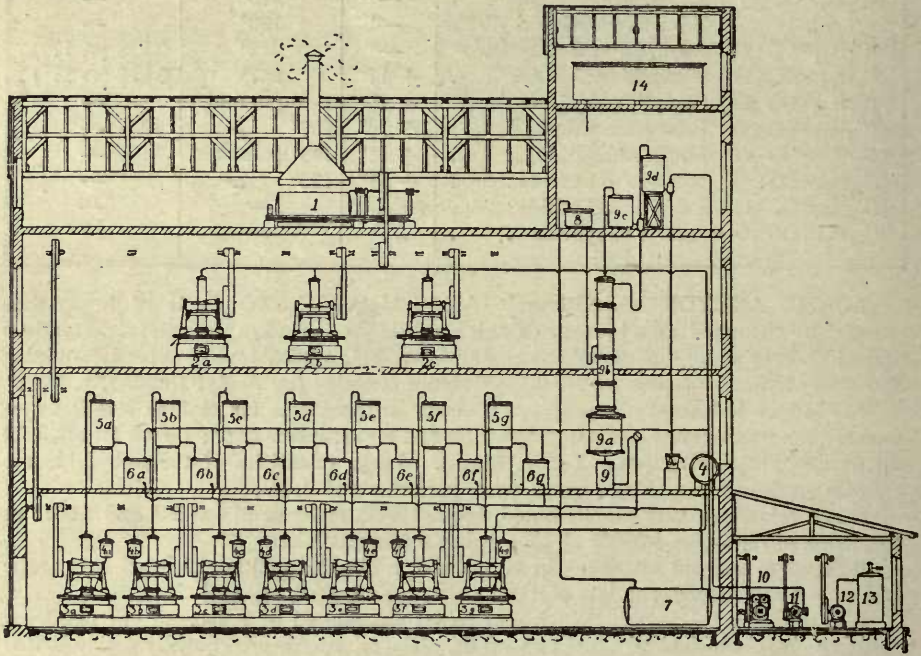

FIG. 253.

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[1] Of the numerous patents for the industrial preparation of acetic anhydride, the following may be mentioned: treatment of sodium or calcium acetate with either sulphuryl chloride or phosphorus oxychloride and CO_2, or a mixture of Cl and SO_2 (Ger. Pats. 161,882, 163,103, and 167,304, 1905); treatment of sodium acetate at 200° with silicon tetrafluoride (Ger. Pats. 171,787 and 171,146, 1906); Ger. Pats. 222,236 and 241,898 (Goldschmidt); Ger. Pats. 244,602 and 273,101 (Afga); Fr. Pat. 17,674, 1913, and Addition 448,342 (Dreyfus); action of $SO_3 + CCl_4$ on sodium or calcium acetate (U.S. Pat. 1,113,927, 1914).

During the European War synthetic acetic acid factories were erected in Great Britain, France and Italy (*see* p. 339), these making acetic anhydride.

Before the war the price of the anhydride in Germany was for large parcels £4–£5 per cwt., and for small amounts, up to £9; the chemically pure product cost £12.

The *anhydrides of di- and poly-basic acids* are not of great importance and are considered to some extent in dealing with the corresponding acids (succinic, pyrocinchonic, etc.); with water they yield the acids with moderate readiness (*see* pp. 365 and 375).

III. HYDROXY-ACIDS

A. SATURATED DIVALENT MONOBASIC ACIDS

These may be regarded as derived from monobasic acids by the replacement of an atom of hydrogen (not that of the carboxyl group) by a hydroxyl group. These acids possess, at the same time, acidic and alcoholic characters and are hence termed *divalent monobasic acids* or *divalent alcohol acids*. The hydroxyl and the carboxyl groups may be substituted at the same time, the compounds then exhibiting the general properties of the acids and alcohols, in addition to new and special characters varying with the position occupied by the carboxyl relatively to the hydroxyl (*see* pp. 355 and 357).

They are usually syrups, which may undergo crystallisation; in comparison with the corresponding fatty acids, the hydroxy-acids are more soluble in water and in alcohol, but less soluble in ether. They do not distil unchanged and often lose water, forming anhydrides.

GENERAL METHODS OF PREPARATION. (*a*) By oxidising dihydric alcohols so as to transform the primary alcoholic group into carboxyl.

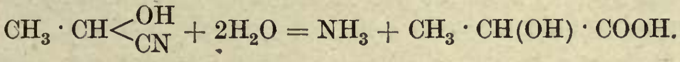
(*b*) By boiling unsaturated acids with sodium hydroxide, so that a molecule of water is added at the double bond.

(*c*) By substituting the halogen of a monohalogenated monobasic acid by hydroxyl; this is effected by treatment with KOH or with silver acetate, the diacetate formed in the latter case being hydrolysed by heating with sodium carbonate :

$$CH_2Cl \cdot COOH + H_2O = OH \cdot CH_2 \cdot CO_2H + HCl.$$

Monochloracetic acid Glycollic acid

(*d*) *a*-Hydroxy-acids are obtained by hydrolysing the nitriles formed on treating the aldehydes or ketones (having one atom of carbon less) with hydrocyanic acid :



$$CH_3 \cdot CH{<}{}^{OH}_{CN} + 2H_2O = NH_3 + CH_3 \cdot CH(OH) \cdot COOH.$$

Ethylidenecyanohydrin

Glycolcyanohydrin, $OH \cdot CH_2 \cdot CH_2 \cdot CN$, yields ethylenelactic acid, $OH \cdot CH_2 \cdot CH_2 \cdot COOH$.

(*e*) By the action of nitrous acid on amino-acids :

$$COOH \cdot CH_2 \cdot NH_2 + NO \cdot OH = H_2O + N_2 + COOH \cdot CH_2 \cdot OH.$$

Glycocoll

(*f*) By reducing aldehydic or ketonic acids :

$$CH_3 \cdot CO \cdot COOH + H_2 = CH_3 \cdot CH(OH) \cdot COOH.$$

Pyruvic acid Lactic acid

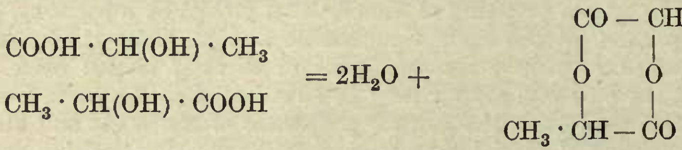
(*g*) By oxidation of acids containing a tertiary carbon atom, $>CH \cdot COOH$, with permanganate.

PROPERTIES AND CONSTITUTION. The constitutions of these acids can always be deduced from the syntheses indicated above. That they contain an alcoholic group is shown by the fact that the hydroxylic hydrogen may be replaced by an alkyl group, giving true *non-hydrolysable ethers*. Similarly the presence of a carboxyl group is shown by the formation of *hydrolysable* *esters.* The isomerism exhibited is the same as with the haloid derivatives of the acids.

The number of alcoholic hydroxyl groups is determined by the *acetyl number* (*see* p. 224). The reactivity, which corresponds with the dissociation constant, increases with the proximity of the hydroxyl to the carboxyl group.

α-, β-, δ-, and *d*-hydroxy-acids are distinguished also by the products resulting from the elimination of one or more molecules of water.

Thus, α-hydroxy-acids, when heated, lose 2 mols. of H_2O per 2 mols. of acid, the hydroxyl group of the one reacting with the carboxyl group of the other; the compound formed is called a *lactide* and is a double ester, which yields the acid again on hydrolysis with hot water or dilute acid:



$$\begin{array}{l} COOH\cdot CH(OH)\cdot CH_3 \\ CH_3\cdot CH(OH)\cdot COOH \end{array} = 2H_2O + \begin{array}{ccc} CO & - & CH\cdot CH_3 \\ | & & | \\ O & & O \\ | & & | \\ CH_3\cdot CH & - & CO \end{array}$$

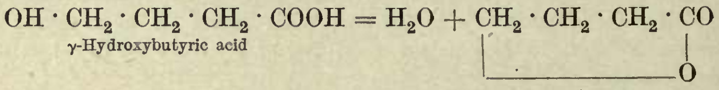
2 mols. Lactic acid

Lactide

Further, α-hydroxy-acids, if heated with sulphuric acid, yield the aldehydes or ketones from which they can originate (*see above*), formic acid being also formed.

The β-acids, however, lose only 1 mol. of water, giving unsaturated acids (*see* p. 352), while, when boiled with 10 per cent. potassium hydroxide solution, they give at the same time $\alpha\beta$- and $\alpha\gamma$-unsaturated acids—a reversible reaction leading to a position of chemical equilibrium; when heated with sulphuric acid they form acids of the acrylic series.

The γ- and δ-acids lose 1 mol. of water, yielding *lactones* (internal anhydrides):



$$OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH = H_2O + \underbrace{CH_2\cdot CH_2\cdot CH_2\cdot CO}_{}\!\!-O$$

γ-Hydroxybutyric acid

Butyrolactone

which are almost always formed when attempts are made to liberate these hydroxy-acids from their salts. The lactones are neutral liquids soluble in water, alcohol, and ether; they distil unchanged and with alkali form the salts of the corresponding hydroxy-acids.

When the hydroxy-acids are heated with hydrogen sulphide, they furnish the corresponding fatty acids.

GLYCOLLIC ACID (Hydroxyacetic or Ethanoloic Acid), **$OH\cdot CH_2\cdot COOH$**, crystallises in needles or plates melting at 80°, and is soluble in water, alcohol, or ether. In nature it is found in immature eggs and in the leaves of the wild vine.

It may be obtained by the general methods given above and also by oxidising alcohol or glycol with dilute nitric acid or by reducing oxalic acid with nascent hydrogen.[1] It is usually prepared by hydrolysing monochloracetic acid with KOH [general method (*c*)].

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[1] Of some interest is the formation of the various *anhydrides* of glycollic acid, these being formed by the removal of 1 mol. of H_2O from 2 mols. of the acid as follows:

(1) From the two alcohol groups, giving a true ether with two free acid groups, $O<\begin{matrix}CH_2\cdot COOH\\ CH_2\cdot COOH\end{matrix}$, *diglycollic acid*, m.-pt. 148°; (2) from the two carboxyl groups; this should give the *anhydride of glycollic acid*, $\begin{matrix}OH\cdot CH_2\cdot CO\\ OH\cdot CH_2\cdot CO\end{matrix}>O$, which is not yet known; (3) from one alcohol and one acid group, giving a true ester, *glycolglycollic acid*, $\begin{matrix}OH\cdot CH_2\cdot CO\\ COOH\cdot CH_2\end{matrix}>O$. Also loss of $2H_2O$ from the two alcoholic and acidic groups gives either (1) *Diglycollic anhydride* (anhydride and ether at the same time), $O<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>O$ (melting at 97° and boiling at 240°), or, when each molecule of water separates from 1 alcoholic and 1 acidic group, (2) the isomeric *glycollide*, $O<\begin{matrix}CH_2\cdot CO\\ CO\cdot CH_2\end{matrix}>O$, melting at 86°.

According to Ger. Pats. 194,038 and 204,787, glycollic acid is now prepared industrially by reducing oxalic acid electrolytically in the following manner: The cathodic liquid consists of a solution of 7 parts of crystallised oxalic acid in 33 parts of water and 11 parts of concentrated sulphuric acid, while the anodic liquid, separated by means of a diaphragm, is 30 per cent. sulphuric acid; the electrodes are of lead and the current density 25–250 ampères per sq. metre of cathode surface. According to Ger. Pat. 257,878 (1912) the acid may be prepared also by heating, for eight to nine hours at 175° to 200° in an autoclave fitted with a stirrer, about 30 parts of trichloroethylene, 50 parts of quicklime, and 250 parts of water, with traces of copper salts as catalyst; with caustic soda the reaction is more rapid:

$$C_2HCl_3 + 4NaOH = H_2O + 3NaCl + OH \cdot CH_2 \cdot CO_2Na.$$

Glycollic acid is now used with advantage to replace tartaric acid in textile printing, as it has a greater solvent action on tannates of dyestuffs, which hence penetrate the fabric better and give more stable colours without injuring the fibre. The ammonium salt of glycollic acid serves to fix dyes on wool, while the aluminium and tin salts are used in alizarin and alizarin orange printing (1914).

Glycollic acid forms a *calcium salt*, $(OH \cdot CH_2 \cdot COO)_2Ca + 3H_2O$, insoluble in water. The most important derivative of glycollic acid is

GLYCOCOLL (Glycine or Aminoacetic or Aminoethanoic Acid), $COOH \cdot CH_2 \cdot NH_2$, which is the first member of the amino-acid series so important to vegetable physiology. It is obtained, together with secondary products, by the action of concentrated ammonia solution on monochloracetic acid:

$$CH_2Cl \cdot COOH + 2NH_3 = NH_4Cl + NH_2 \cdot CH_2 \cdot COOH.$$

It is always formed in the decomposition of hippuric acid (benzoylglycocoll) with HCl, or by the action of acid or alkali on gelatine.

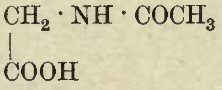
It may also be obtained by the reduction of ethyl cyanocarboxylate by means of nascent hydrogen or from cyanogen and boiling hydriodic acid.

Its homologues are prepared synthetically in various ways, *e. g.*, by treating aldehyde-ammonias with hydrocyanic acid and hydrolysing the amino-cyanides thus obtained with HCl.

Glycocoll crystallises in rhombic columns soluble in 4 parts of water but insoluble in alcohol or ether; it has a sweetish taste and melts and decomposes at 230°.

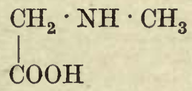
The fact that the amino-group cannot be expelled by hydrolysis establishes the structure of glycocoll. It behaves as both acid and base, forming salts with acids and also with bases. Its copper salt separates in large, dark blue needles on dissolving cupric oxide in hot glycocoll solution: $(C_2H_4O_2N)_2Cu + H_2O$. With ferric chloride it gives an intense red coloration. When heated with baryta, it loses CO_2, forming methylamine; with nitrous acid it gives glycollic acid.

Various *alkyl* and other derivatives have been obtained synthetically from glycocoll:



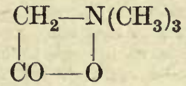
$$\begin{array}{l} CH_2 \cdot NH \cdot COCH_3 \\ | \\ COOH \end{array}$$

Aceturic acid



$$\begin{array}{l} CH_2 \cdot NH \cdot CH_3 \\ | \\ COOH \end{array}$$

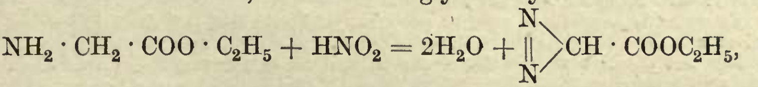
Sarcosine
(derived from caffeine and from creatine)



$$\begin{array}{l} CH_2—N(CH_3)_3 \\ |\qquad\quad | \\ CO—O \end{array}$$

Betaine
(from the beet)

With nitrous acid, the esters of glycocoll yield **ETHYL DIAZOACETATE**,



$$NH_2 \cdot CH_2 \cdot COO \cdot C_2H_5 + HNO_2 = 2H_2O + \begin{array}{c} N \\ \| \\ N \end{array}\!\!>\!CH \cdot COOC_2H_5,$$

which is a yellow oil boiling at 141° and readily decomposes and reacts with evolution of nitrogen; it serves for the synthesis of pyrazole.

LACTIC ACIDS, $OH \cdot C_2H_4 \cdot CO_2H$

The two structural isomerides foreseen by theory are known: α- and β-hydroxypropionic acids. Also the α-acid exists in two stereoisomeric forms (l = lævo- and d = dextro-rotatory) owing to the presence of an asymmetric carbon atom (p. 19) and in an inactive form (i = inactive), consisting of a mixture in equal proportions of the two stereoisomerides. These lactic acids form *anhydrides* similar to those of glycollic acid (*see above*).

The lactic acids give Uffelman's *reaction*, that is, they cause the amethyst-coloured solution obtained on adding a drop of ferric chloride to a dilute salicylic acid solution to turn yellow; this reaction is given also by citric, oxalic, and the tartaric acids.

(1) **i-ETHYLIDENELACTIC ACID** ($l + d$) **(2-Propanoloic or a-Hydroxypropionic Acid or Ordinary Lactic Acid of Fermentation), $CH_3 \cdot CH(OH) \cdot COOH$,** is found in milk rendered acid by the action of the *lactic acid bacillus* (*see* Fig. 116, p. 145), in milk-sugar (also cane- and grape-sugars, gum, starch, etc.) which undergoes acid fermentation (*lactic fermentation*) even in absence of air, although oxygen facilitates the change. Cabbage fermented with vinegar and salt (Sauerkraut), gastric juice, putrefied cheese, fresh fodder siloed, and fermented muscular juices and the brain [1] also contain free lactic acid.

When pure it melts at 18° and boils at 120° under 12 mm. pressure, but usually it forms a dense syrup soluble in water, alcohol, or ether. It is optically inactive, as it consists of a *racemic* mixture of dextro- and lævo-acids (*see* p. 21). The two modifications may be separated by crystallisation of the strychnine salts or by cultivating in the solution *Penicillium glaucum*, which first destroys the lævo-acid (*see* p. 23). When heated, the active acid is transformed, to the extent of one-half, into the optical enantiomorph, so that the inactive racemic acid is obtained. If kept in a desiccator, it is partly converted into anhydride owing to loss of water. When distilled under reduced pressure, it yields water, carbon dioxide, and lactide (*see above*). If heated with dilute sulphuric acid it decomposes, like many other a-hydroxy-acids, into acetaldehyde and formic acid.

PREPARATION. Of the various processes for the preparation of lactic acid,[2] only

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[1] It appears now to be proved that the lactic acid in the human organism is formed in proportion to the muscular and cerebral work, and, together with carbon dioxide, which is also a waste product of the cells of the organism during wakefulness, produces *sleep*. While we sleep, the blood carries off these waste products more easily, the cells then recovering their function and their sensibility. The connection between sleep and fatigue is well known, and is shown not only by the fact that after great muscular or cerebral fatigue sleep is more profound, but by the results of the following experiment: if the blood of a very tired dog is injected into the veins of another dog in a normal state, this dog soon exhibits signs of great fatigue and goes to sleep; these results are not observed if the blood injected is that of a non-fatigued dog. During heavy muscular labour, the air expired contains more CO_2 than in a state of repose and more still than during sleep. The carbon dioxide diminishes the oxygen so much needed by the muscles and brain, so that the activity of these remains depressed. As is well known, lactic acid has a depressing action on the nervous cells, injection of the acid into the veins of any person inducing symptoms of fatigue and sleepiness and finally sleep. The continuance of sleep is due to the fact that the blood flows more slowly to the brain, to which it hence carries less oxygen. It appears, indeed, to be proved that in general five or six hours' sleep—very deep for two hours—is sufficient for the blood to wash away these waste products of active cellular work and to restore activity to all the cerebral centres.

[2] Kiliani treats 500 grams of inverted sugar with 250 grams of water and 15 grams of sulphuric acid at 50° to 60° for two hours, and then adds gradually 400 c.c. of concentrated caustic soda solution (1 : 1), the liquid being kept boiling meanwhile.

The soda is subsequently neutralised with 50 per cent. sulphuric acid and the solution left for twenty-four hours to deposit crystalline sodium sulphate. The lactic acid is extracted with alcohol—which does not dissolve the sulphate—the alcohol being recovered by distillation. The crude lactic acid remaining is diluted, saturated with zinc carbonate and evaporated; the zinc lactate is then allowed to separate, and is filtered off, redissolved in hot water and decomposed with H_2S. After filtration, the liquid is concentrated *in vacuo*, pure lactic acid being thus obtained.

Various other methods have been tried. For instance, 3 kilos of cane-sugar and 15 grams of tartaric acid are dissolved in 13 litres of boiling water. In a few days' time, after the cane-sugar has been converted into glucose and levulose, 4 litres of acid milk and 100 grams of putrefied cheese (also 1·5 kilos of zinc carbonate to fix the lactic acid, which otherwise would arrest the lactic fermentation) are added and the mixture left for a week at a temperature of 40° to that used industrially on a large scale will be described, since for some years the manufacture from whey has been abandoned owing to the low yields, the difficulty of eliminating the salts and various organic compounds, and the facility with which contamination by butyric organisms occurs.

Use is now always made of starchy materials, especially of potato starch, which is intimately mixed with two parts of cold water, the mixture being well stirred and treated with six parts of boiling water until a slightly opalescent liquid free from even the smallest lumps is obtained. The mass is cooled in a vat to 60° and treated with the diastase solution (green malt equal in amount to 15 per cent. of the weight of the starch is macerated and occasionally shaken during three hours with four times its weight of water at the ordinary temperature, the filtered liquid then containing the diastase); the saccharification of the starch is carried out at 55° to 60° and finally at 65°, until the iodine reaction for starch fails. The wort thus obtained (*see also:* Manufacture of Alcohol, pp. 143, 201) is treated with 50 per cent. of powdered calcium carbonate, 5 per cent. (on the weight of the starch) of sterilised skim milk and with wort (1 litre per 100 litres) from a vat in which a pure lactic acid organism (a little *Bacillus Delbrücki* may be added) is actively developing. The temperature is kept at 40° to 50°, and the mass is vigorously mixed two or three times per day so that the lactic acid may be fixed by the calcium carbonate; after a week crusts of calcium lactate begin to separate. The fermentation is continued for three to four days longer, until indeed a sample of the liquid, freed from chalk and carbonic acid, ceases to reduce Fehling's solution (*see later:* Sugars).

This fermentation consists solely of a decomposition, $C_6H_{12}O_6 = 2C_3H_6O_3$, and is accompanied by neither generation of CO_2 nor absorption of water.

In the fermenting rooms the greatest cleanliness is necessary, in order to prevent infection with extraneous bacteria. If such infection (recognisable by the bad smell and by lack of the crystalline crusts of calcium lactate, so that fine granules of calcium carbonate alone are visible when the liquid is stirred) does occur in any vat, the contents of the latter should be boiled to sterilise it and the lactic fermentation again started at 55° to 60°.

45°, by which means the maximum production of lactic acid is obtained. The acid separates as zinc lactate in crystalline crusts which, after purification (by recrystallisation), are suspended in water and decomposed with H_2S in order to remove the zinc as insoluble sulphide. The filtered liquid is concentrated to a syrupy consistency and then extracted with ether, which does not dissolve the impurities (zinc salts, mannitol, etc.); on evaporation of the ether, pure syrupy lactic acid is obtained. Besides the decomposition of the sugar, various secondary reactions always accompany lactic fermentation, and the yield of the acid is scarcely 20 per cent. of the weight of the sugar taken.

A better yield is, however, obtained by Larrieu's process (Fr. Pat. 206,506), which consists in treating starch paste with malt and hot water (as in the ordinary industrial process).

Jacquemin prepares the acid from worts similar to those employed in breweries (barley mashed at 50° with malt, then boiled to destroy the diastase and cooled to 45°) by the addition of pure lactic ferment and calcium carbonate. After five to six days, the mash is filtered and concentrated, the calcium lactate being then decomposed in the usual way with sulphuric acid.

Dreher works in a similar manner, but with glucose solutions containing 1 per cent. of nutrient substances for the ferment (*e. g.*, sodium phosphate, nitre, salt, etc.).

Industrially, however, lactic acid was formerly always obtained from milk residues (*whey* or *molasses* of milk-sugar, which remain after the removal of the butter from the milk in the separator; also cheese by coagulation with rennet in the hot). The whey is concentrated in open vessels or, better, in vacuum pans, to 16° Bé., and is then introduced into wooden vessels in which, at a temperature of 40°, the lactic ferment is added in the form either of part of the liquid from a previous fermentation or of putrefied cheese. Powdered chalk is added to neutralise the acid formed, the liquid being stirred from time to time and the fermentation allowed to continue for ten to twelve days. After decantation, the calcium lactate is decomposed with dilute sulphuric acid, the liquid mass being well mixed, and the iron separated if necessary by means of potassium ferrocyanide. In some cases, before the calcium lactate is decomposed, it is separated by concentrating the solution, and is recrystallised from a little hot water, which should dissolve 20 per cent. of it, and then treated as usual with dilute sulphuric acid. The calcium sulphate formed is removed by passing the mass through a filter-press (*see* figure in the section on Sugar) and the clear lactic acid solution concentrated in a double- or triple-effect apparatus until it attains a concentration of 50 per cent. The further small quantity of gypsum which is then deposited is separated by filtration, the resulting yellowish-brown liquid representing commercial, crude, 50 per cent. (by weight) lactic acid. This should not contain more than 1·5 per cent. of ash, and should not contain sulphate or reduce Fehling's solution.

The lactic acid prepared from the molasses of milk-sugar factories is more impure than the above.

Lactic acid is also obtained (1905) from a mixture of bran and barley.

At the end of the fermentation the liquid is rendered alkaline by addition of milk of lime, boiled with decolorising charcoal, and filtered hot through filter-presses, the calcium lactate crystallising out on cooling (in some factories the calcium lactate solution is decomposed directly by means of sulphuric acid, the liquid being boiled with charcoal and potassium ferrocyanide—to expel iron—filtered and boiled to syrupy lactic acid). The calcium lactate crystals are collected in a vacuum-filter, the mother-liquors being reconcentrated and the crystals, dissolved in boiling water, treated with pure sulphuric acid until the liquid colours Congo red paper deep violet (showing excess of mineral acid) and filtered to remove the calcium sulphate. The colourless liquid is concentrated in a vacuum apparatus (lead-lined or enamelled) to a strength of 50 per cent. The wash-waters from the calcium sulphate serve for making the milk of lime. From 100 kilos of starch 135 kilos of commercial 50 per cent. lactic acid is obtainable, but this contains also other organic acids and at 200° leaves a residue of 5 to 6 per cent.; with further purification the yield diminishes. If the heating is too prolonged during the concentration, lactide is formed to some extent.

Very *pure* lactic acid is obtained by extracting the crude product with ether or amyl alcohol—which does not dissolve the impurities (sugar, gum, mineral substances)—and steam-distilling *in vacuo.*

An English patent (No. 26,415, 1907) describes the preparation of pure, concentrated lactic acid by the distillation of the commercial 50 per cent. acid in a rapid current of air or of an indifferent gas.

In some cases purification is effected by crystallisation of the zinc salt.

USES. Until a few years ago the uses of lactic acid were limited to the preparation of soluble lactates for medicinal purposes, but its manufacture has recently been considerably extended owing to its employment in the dyeing of wool, silk, etc., in place of tartaric acid, tartar and oxalic acid for the reduction of the chromium compounds with which wool to be treated with fast dyes (alizarin dyes, etc.) is mordanted. For the same reasons it is advantageously employed in the chrome tanning of skins, its value in this case being sometimes regarded as due to its ability to keep calcium salts in solution and thus prevent the formation of certain white harmful deposits.

The crude 50 per cent. acid is most commonly sold, and it is necessary to ascertain whether by 50 per cent. is meant 50 kilos per 100 litres or per 100 kilos of solution; in the former case the strength of the acid is only 43 per cent. by weight (*i. e.*, 100 kilos contain 43 kilos of acid).

Commercial, brown, 50 per cent. lactic acid cost about 32*s.* per cwt. before the war; the paler, yellow product of the same strength, 52*s.*; the pure (sp. gr. 1·21), 3*s.* 7*d.* per kilo, and the chemically pure, 12*s.* per kilo.

Before the war importation of lactic acid into Italy was subject to a duty of 6*s.* per cwt. The amounts of the Italian imports and exports are as follows (tons):

	1908	1910	1912	1913	1914	1915	1916	1917	1918
Importation .	65	49	40	51	40	10·7	0·9	0·8	0·2
Exportation .	—	—	4·8	4·6	0·5	8	—	0·1	—
French importation	—	—	—	155	156	72	89	—	—

Before the war Germany exported the following quantities of lactic acid and lactates:

	1909	1910	1911	1912	1913
Tons	1044	1278	1807	1771	2049

Salts of Lactic Acid are generally soluble to some extent in water. *Calcium lactate*, $(C_3H_5O_3)_2Ca + 5H_2O$, forms mammillary aggregates of white needles soluble in 9·5 parts of cold water, and in all proportions in boiling water; it is insoluble in cold alcohol. The water of crystallisation is evolved in a vacuum desiccator or on heating to 100°. At 250° it loses H_2O, giving *calcium dilactate*, which is less soluble in alcohol than the original salt.

Calcium lactophosphate, obtained by neutralising lactic acid with gelatinous calcium phosphate, dissolves to some extent in water and is used for treating rickets and diseases of the bones. *Ferrous lactate*, $(C_3H_5O_3)_2Fe + 3H_2O$, is obtained by treating boiling aqueous calcium lactate solution with ferrous chloride solution, greenish-yellow crystals separating on cooling; it is used in medicine. *Zinc lactate* crystallises with $3H_2O$.

ALANINE, $CH_3 \cdot CH(NH_2) \cdot COOH$, is obtained from the corresponding aldehyde-ammonia by the action of hydrocyanic acid. From the inactive, synthetic compound, the active stereoisomerides are separated by means of the strychnine or brucine salts. The action of PCl_5 expels both the hydroxyl- and the amino-groups, giving *lactyl* chloride, $CH_3 \cdot CHCl \cdot COCl$, which gives *a*-chlorpropionic acid, $CH_3 \cdot CHCl \cdot COOH$, when treated with water.

(2) *d*-**ETHYLIDENELACTIC ACID** (Paralactic or Sarcolactic Acid) differs from ordinary lactic acid only in the greater solubility of its zinc salt ($+ 2H_2O$), and the less solubility of its calcium salt ($+ 4H_2O$). It is found in Liebig's extract of meat, and it is contained in the muscular juices, and is also formed in certain lactic fermentations.

(3) *l*-**ETHYLIDENELACTIC ACID** is formed during the fermentation of aqueous cane-sugar solutions by *Bacillus acidi lævolactici.*

(4) **ETHYLENELACTIC ACID** (Hydracrylic, β-Hydroxypropionic or 3-Propanoloic Acid), $OH \cdot CH_2 \cdot CH_2 \cdot COOH$, differs from its isomerides in that, when heated, it loses a molecule of water, giving, not the anhydride, but acrylic acid, $CH_2 : CH \cdot CO_2H$. Further, with oxidising agents it gives, not acetic acid, but oxalic acid and carbon dioxide. It contains no asymmetric carbon atom and is hence optically inactive. It may be prepared synthetically from (1) β-iodopropionic acid, or (2) ethylene, $CH_2 : CH_2$, by addition of hypochlorous acid, giving $OH \cdot CH_2 \cdot CH_2Cl$, which is then converted into the nitrile $OH \cdot CH_2 \cdot CH_2 \cdot CN$, hydrolysis of the latter giving ethylenelactic acid. The acid is a colourless, syrupy liquid and forms a calcium salt ($+ 2H_2O$) and a readily soluble zinc salt ($+ 4H_2O$).

HYDROXYBUTYRIC ACIDS, $OH \cdot C_3H_6 \cdot CO_2H$

Five isomerides are theoretically possible, four being known: two *a-acids*, one *β-acid*, and one *γ-acid* (prepared only as salts).

α-**HYDROXYBUTYRIC ACID**, $CH_3 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, melts at 43° and is synthesised as the inactive, racemic form, which may be resolved into its active components by means of brucine (*see* p. 23).

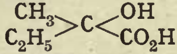
α-**HYDROXYISOBUTYRIC ACID** (Acetonic or 2-Methyl-2-propanoloic Acid), $OH \cdot C(CH_3)_2 . CO_2H$, melts at 79°, boils at 212°, and is obtainable by various synthetical methods from dimethylacetic acid, acetocyanohydrin, α-aminobutyric acid, etc.

β-**HYDROXYBUTYRIC ACID**, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, is obtained by oxidising aldol or reducing acetoacetic acid, these methods of formation indicating its constitution. It forms a syrup and its lævo-isomeride is found in the blood and in diabetic urine.

HIGHER HYDROXY-ACIDS

α-**HYDROXYVALERIC ACID**, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, melts at 29°.

α-**HYDROXYISOVALERIC ACID**, $(CH_3)_2CH \cdot CH(OH) \cdot CO_2H$, melts at 86°.

METHYLETHYLGLYCOLLIC ACID,  $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!>\!C\!<\!\begin{matrix} OH \\ CO_2H \end{matrix}$, melts at 68°.

α-**HYDROXYCAPROIC ACID** (Leucinic Acid), $CH_3 \cdot [CH_2]_3 \cdot CH(OH) \cdot CO_2H$, melts at 73° and is obtained from leucine (*see later*).

α-**HYDROXYMYRISTIC ACID**, $CH_3 \cdot [CH_2]_{11} \cdot CH(OH) \cdot CO_2H$, melts at 51°.

α-**HYDROXYPALMITIC ACID**, $CH_3 . [CH_2]_{13} . CH(OH) \cdot CO_2H$, melts at 82°.

α-**HYDROXYSTEARIC ACID**, $CH_3 \cdot [CH_2]_{15} \cdot CH(OH) \cdot CO_2H$, melts at 84° to 86°, and is formed by the action of cold concentrated sulphuric acid on oleic acid, this method being sometimes used practically to prepare solid fatty acids from liquid oleic acid (*see* section on Fats).

The Sulphuric Ether of α-Hydroxystearic Acid, $C_{18}H_{35}O_2(OSO_3H)$, is used in the dyeing of cotton with Turkey-red (*see below*).

Various other β-hydroxystearic and dihydroxystearic acids, with melting-points higher than those of the liquid fatty acids which yield them, are also known.

B. MONOBASIC UNSATURATED HYDROXY-ACIDS

The α-Hydroxyolefinecarboxylic Acids are prepared by hydrolysing, with HCl in the cold, the nitriles obtained by the addition of hydrogen cyanide to olefinic aldehydes. If the double linking (Δ) is in the $\beta\gamma$-position, these hydroxy-acids are converted into γ-ketocarboxylic acids when boiled with dilute HCl; thus, *a*-hydroxypentenoic acid, $CH_3 \cdot CH : CH \cdot CH(OH) \cdot CO_2H$, yields levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

Several **β-Hydroxyolefinecarboxylic Acids** are known. The most simple is *β-hydroxyacrylic* or *formylacetic acid*, $CO_2H \cdot CH : CH \cdot OH$, which, like the others, readily forms esters and halogen derivatives.

γ- and δ-Hydroxyolefinecarboxylic Acids are known mostly in the form of *lactones* (*see* pp. 355 and 384).

RICINOLEIC ACID (Hydroxyoleic Acid), $C_{18}H_{34}O_3$, or $CH_3 \cdot [CH_2]_5 \cdot CH(OH)_2$ $CH_2 \cdot CH : CH \cdot [CH_2]_7 \cdot CO_2H$, constitutes, in the form of glyceride, the greater proportion of castor oil, and, on dry distillation under reduced pressure, decomposes into œnanthaldehyde, $C_7H_{14}O$, and undecylenic acid, $C_{11}H_{20}O_2$. It solidifies at − 6° and melts at + 4°. It forms lead and barium salts soluble in ether, and, when fused with KOH, yields sebacic acid, $C_8H_{16}(CO_2H)_2$, and sec. octyl alcohol. It forms a solid bromide and an oily ozonide (by the addition of ozone) which decomposes, giving, among other products, a large proportion of azelaic acid (Molinari and Caldana, 1909), the position of the double linking—established by Goldsobel (1894) by means of ricinostearolic acid—being thus confirmed. By nitrous acid it is transformed into the isomeric *ricinelaidinic acid*, melting at 53°. By decomposing the ozonide of methyl ricinoleate, Haller and Brochet (1910) obtained *β-hydroxypelargonic acid*, $CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CO_2H$, azelaic acid and the corresponding semi-aldehyde.[1]

By treating castor oil slowly with cold, concentrated sulphuric acid, *ricinosulphuric acid* is obtained, this being the most important constituent of Turkey-red oil, which is used in large quantities in the dyeing and printing of cotton textiles with alizarin red (*Adrianople red*).[2] It is also used for greasing wool to be spun and for dressing textiles.

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[1] **Ricinoleic Acid** was prepared pure by Krafft (1888) by hydrolysing castor oil, the fatty acids thus obtained being cooled at 0° and the solid acids separated by squeezing (at 10°). The dry lead or barium salt was then prepared and extracted with ether, which leaves undissolved the last traces of the salts of the solid fatty acids; the salt of ricinoleic acid is dissolved and gives the pure acid.

With concentrated sulphuric acid, the acid gives (Benedikt and Ulzer, 1887; Juillard, 1894 and 1895; Chonowsky, 1909, and especially Ad. Grün, 1906 and 1909) *ricinoleinsulphonic acid* $C_{17}H_{32}(O \cdot SO_3H) \cdot CO_2H$; by hot water this acid is hydrolysed with separation of sulphuric acid and formation of a condensed ester (*ricinoleinricinoleic ester*), $C_{17}H_{32}(OH) \cdot CO \cdot O \cdot C_{17}H_{22} \cdot CO_2H$, the condensation taking place between the carboxyl group of one molecule and the hydroxyl of another; only one acetyl group is introduced into the molecule of this compound by the action of acetic anhydride. Various isomeric condensed anhydrides of dihydroxystearic acids are also easily prepared: these are solid and have the constitution $C_{17}H_{33}(OH)_2 \cdot CO \cdot O \cdot C_{17}H_{33}(OH) \cdot CO_2H$ (4 isomerides) and may be converted into the corresponding *dihydroxystearic acids*. One of the latter melts at 90° and is optically active ($[\alpha]_D = + 6{\cdot}45°$), two melt at 69·5° and 108° respectively and are inactive, while the fourth melts at 126° and is active; the positions of the two hydroxyl groups seem to be 9 and 12, or 10 and 12 (for those with the higher melting-points).

The action of sulphuric acid on *olive oil* partly decomposes the triolein into glycerol and oleic acid and partly transforms it only into diolein. To some extent the double linking of oleic acid fixes H_2O and forms hydroxystearic acid, which is partly converted into the *sulphuric ester of* 1 : 10-*dihydroxystearic acid*. Besides free ricinoleic acid, undecomposed glycerides and glycerol, Turkey-red oil contains (according to Juillard), the sulphuric ester of ricinoleic acid, dihydroxystearic acid and the two corresponding mono- and di-sulphuric esters, as well as diricinoleic acid and other polymerides (up to *pentaricinoleic acid*).

The phenomenon of polymerisation is, indeed, of great importance as regards the effects produced in practice by the sulphoricinate.

[2] **Turkey-Red Oil** (or *sulphoricinate*) is prepared by treating castor oil—in an open, double-bottomed, iron vessel furnished with a stirrer—with 20 per cent. (in summer) or 25 per cent. (in winter) of concentrated sulphuric acid (66° Bé.), which is added very slowly during five or even eight hours, so that the temperature of the mass never exceeds 35°; if these precautions are neglected, SO_2 is evolved. When necessary, the temperature is moderated by passing cold water through the jacket. The mixture is left for some hours until a small portion is found to be soluble in water. The mass is then discharged into a wooden vat containing a quantity of sodium chloride or sulphate equal to that of the oil treated. After mixing, the liquid is allowed to stand for some hours, the excess of acid (10 to 12 per cent. is fixed in the sulphoricinate) being next removed by decanting the aqueous portion and washing the remainder in the same manner and afterwards with two successive quantities of water half saturated with common salt; sufficient concentrated ammonia or sodium hydroxide solution is then added to give a neutral (or amphoteric) reaction. The quantity and concentration of the alkali to be added are determined by a preliminary test on a small portion, which gives also the content in fatty acids of the commercial ricinate. It is usually a clear, yellowish solution, which gives

The treatment of castor oil with concentrated sulphuric acid yields ricinoleic acid more or less polymerised or condensed into anhydrides, glycerolsulphuric esters of ricinoleic acid and a preponderating proportion of ricinosulphuric acid, which is an ester of sulphuric acid soluble in water : $C_{18}H_{33}O_2 \cdot OH + H_2SO_4 = H_2O + C_{18}H_{33}O_2 \cdot O \cdot SO_3H$. This acid is separated from water by addition of salt or dilute mineral acid in the cold; it is only slightly soluble in ether, and its calcium, lead, etc., salts are insoluble in water. Ricinosulphuric acid is not decomposed in the hot by water or dilute alkali, but it decomposes readily into sulphuric and ricinoleic acids when boiled with dilute hydrochloric or sulphuric acid. By using an excess of concentrated sulphuric acid, Grün (1907) obtained 9 : 12-dihydroxystearic acid. Ricinosulphuric acid or its sodium or ammonium salt is of importance in Turkey-red oil, since, when the latter is diluted with water, it serves to keep in a state of solution the castor oil or other unaltered oil always found in greater or larger quantity in Turkey-red oil.

Treatment of olive oil or oleic acid with sulphuric acid yields hydroxystearosulphuric acid, which is *saturated*, $C_{18}H_{34}O_2$ (oleic acid) $+ H_2SO_4 = C_{18}H_{35}O_2 \cdot O \cdot SO_3H$; so that the iodine number may be used to distinguish true sulphoricinates from saturated ones, which are unable to undergo those characteristic oxidations necessary to dyeing operations. With an excess of sulphuric acid, hydroxystearosulphuric acid takes up a molecule of water, yielding sulphuric acid and hydroxystearic acid (saturated), $C_{18}H_{35}O_2 \cdot OH$.

C. POLYVALENT MONOBASIC HYDROXY-ACIDS

These are derived from polyhydric alcohols by the oxidation of one primary alcoholic group to carboxyl, the other two or more alcoholic groups remaining unaltered; they exhibit behaviour analogous to that of lactic acid. The number of the hydroxyls is deduced from the acetyl number (*see* p. 224). These acids, which are gelatinous and crystallise with difficulty, are sometimes obtained by the gradual oxidation of saccharine substances or of unsaturated acids.

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a clear solution when diluted with 2 to 4 vols. of water and a milky emulsion when mixed with 5 to 6 vols. of water or with dilute alkali.

The commonest strengths are 40, 50, and 60 per cent. of *total fat* (liberated from the alkali), which is estimated by Herbig's method (1906); 10 grams of the sulphoricinate are dissolved in 50 c.c. of hot water, 25 c.c. of dilute HCl being then added and the solution boiled for four or five minutes, during which time it is kept stirred to avoid spurting. It is next cooled (and, if desired, the *volume* of the washed fatty acids may be measured in a burette) and extracted in a separating funnel with 200 c.c. of ether, which is washed with three separate quantities of 15 to 20 c.c. of water. The ether is distilled off from a tared flask, the fat being heated over a naked flame and shaken for a couple of minutes, dried at 105° for half an hour and weighed. When neutral, not sulphonated, fats are present, they are determined by treating 30 grams of the sulphoricinate with 50 c.c. of water, 20 c.c. of ammonia, and 30 c.c. of glycerol, the whole being extracted with ether, which is washed with water and evaporated in a tared dish. To ascertain if the sulphoricinate is the ammonium or sodium compound, tests are made for these bases in the wash-water separated in estimating the total fat; the ammonia is estimated by heating with excess of alkali and collecting the ammonia in a standard solution of sulphuric acid, while the soda is determined by evaporating to dryness, calcining the residue and weighing as sodium sulphate.

If the sulphoricinate were not prepared from castor oil (inferior products are obtained from olive oil with a larger amount of sulphuric acid), it will give a turbid solution in alcohol, while the *acetyl number* (*see* p. 224) of the *total fat* is only 5 to 10 (for olive oil), that of true sulphoricinate being usually 140 and always above 125. Further, the iodine number of the acids of true sulphoricinate is never lower than 68 to 70, whilst with other oils it is decidedly lower than 70. In the Zeiss oleorefractometer the fatty acids of pure sulphoricinate give a reading of 74.

The complete analysis of a good sulphoricinate gave 58 per cent. of total fat (composed of 47 per cent. of insoluble fatty acids, 1·5 per cent. of neutral fats, and 9·5 per cent. of fatty sulpho-acids soluble in water), 1·8 per cent. of ammonia, and 4·6 per cent. of sulphuric acid. In true sulphoricinates, however, the ratio of sulphuric to sulphoricinic acid should be not 4·6 : 9·5, but rather 4·6 : 22, and the sulphuric acid as sodium or ammonium sulphate should not exceed 0·2 to 0·3 per cent. The soluble sulpho-acids are estimated by treating 10 grams of the total fatty acids with (not more than) 10 c.c. of ether and 30 c.c. of saturated sodium chloride solution free from sulphates; the mixture is shaken and filtered through a moist filter, the sulpho-acids in the filtrate being precipitated with barium chloride.

The price of Turkey-red oil is based on its content of total fat and is usually about 10*d*. per unit of fat per 100 kilos of sulphoricinate. This content is often determined in a graduated burette, by decomposing a given quantity of the sulphoricinate with sulphuric acid, diluting with water and measuring, in the burette, the fat which rises to the surface after some hours.

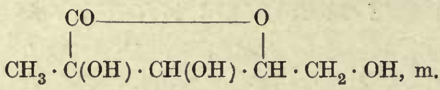
GLYCERIC ACID (αβ-Dihydroxypropionic or Propandioloic Acid), $OH \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, obtained by oxidising glycerol with nitric acid, exists in optically active forms,[1] and is soluble in alcohol, water, or acetone (which does not dissolve glycerol).[2] As has already been mentioned, *dihydroxystearic acid*, $C_{18}H_{34}O_2(OH)_2$, is formed by oxidising oleic acid.

ERYTHRIC ACID (Butantrioloic Acid), $OH \cdot CH_2 \cdot [CH(OH)]_2 \cdot CO_2H$, is formed on gentle oxidation of fructose or erythritol, and is monobasic and tetravalent.

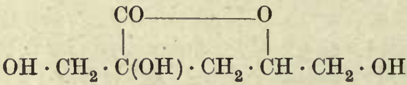
Of the pentavalent monobasic acids, four pentonic or *pentantetroloic* isomerides, $C_4H_5(OH)_4 \cdot CO_2H$, are known, namely: **Arabonic acid** (by oxidising arabinose) is lævorotatory (— 73·9°), melts at 89° and yields a lactone, $C_5H_8O_5$, m.-pt. 95° to 98°, when its solution is evaporated. *d-Arabonic acid* (+ 73·7°) melts at 98°; *l-ribonic acid* yields a lactone, m.-pt. 72° to 76°. *l-Xylonic acid* is formed by prolonged treatment of l-xylose with bromine water; if heated with pyridine it is converted into *d-lyxonic acid*, the lactone of which melts at 162°.

The group of *saccharinic acids* comprises a number of *tetrahydroxypentancarboxylic acids*, which are readily transformed into lactones termed *saccharins* (not to be confused with the saccharin of the aromatic series).

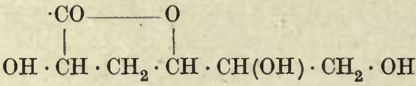
Saccharinic or hexantetroloic acid, $C_5H_7(OH)_4 \cdot CO_2H$, is obtained by treating glucose or fructose with lime, while *iso-* and *meta-saccharinic acids* are also known in the free state and *para-saccharinic acid* as salts. The corresponding lactones are:



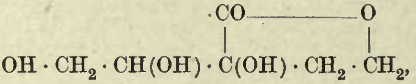
1. *Saccharin*, $CH_3 \cdot C(OH) \cdot CH(OH) \cdot CH \cdot CH_2 \cdot OH$, m.-pt. 160°, has a bitter taste.



2. *Isosaccharin*, $OH \cdot CH_2 \cdot C(OH) \cdot CH_2 \cdot CH \cdot CH_2 \cdot OH$, melts at 95°.



3. *Metasaccharin*, $OH \cdot CH \cdot CH_2 \cdot CH \cdot CH(OH) \cdot CH_2 \cdot OH$, melts at 141°.



4. *Parasaccharin*, $OH \cdot CH_2 \cdot CH(OH) \cdot C(OH) \cdot CH_2 \cdot CH_2$, is a syrupy liquid.

These lactones are distinguished by the different products they form on oxidation with nitric acid or hydrogen peroxide.

The hexonic acids or hexanpentoloic acids, $C_5H_6(OH)_5 \cdot CO_2H$, are known in some cases only as lactones and are obtained by reduction of the corresponding dibasic acids (saccharic acid, etc.) or by gentle oxidation (with bromine water) of the corresponding sugars (hexoses), to which they are closely related:

Mannose, $C_6H_{12}O_6$,	yields		*mannonic acid*,	$C_6H_{12}O_7$.	
Galactose	,,	,,	*galactonic*	,,	,,
Glucose	,,	,,	*gluconic*	,,	,,
Gulose	,,	,,	*gulonic*	,,	,,
Idose	,,	,,	*idonic*	,,	,,
Talose	,,	,,	*talonic*	,,	,,

These acids may be obtained synthetically by hydrolysing the nitriles (*see* pp. 237 and 320) of the simpler sugars (pentoses).

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[1] From the racemic form, the lævo-modification may be obtained by fermenting the ammonium salt with *Penicillium glaucum*, and the dextro-form by the direct action of *Bacillus ethaceticus*.

[2] It forms a calcium salt, $(C_3H_5O_4)_2Ca + 2H_2O$, soluble in water, whilst the lead salt is only slightly soluble in cold water. Among the derivatives of this acid are *serine*, $OH \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, which, being an amino-derivative, has a neutral reaction and forms salts with both acids and bases; it is obtained by boiling silk-gum with dilute sulphuric acid and is soluble in water but insoluble in alcohol or ether.

Among the higher derivatives are (1) ornithine (*αδ-diaminovaleric acid*), $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, which is formed on decomposition of *arginine*, contained in germinating lupins, and (2) lysine, or *αε-diaminocaproic acid*, $NH_2 \cdot [CH_2]_4 \cdot CH(NH_2) \cdot CO_2H$, which is obtained on decomposing casein or glue with hydrochloric acid.

Further, the hexonic acids yield the sugars on reduction, or the dibasic acids on oxidation with nitric acid.

These acids may be separated one from another by the phenylhydrazine reaction; all of them have the same constitution, but they differ in the spacial arrangement of the groups composing the molecule, since they are stereoisomerides containing various asymmetric carbon atoms:

$$OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CO_2H,$$

and for each of these acids, except talonic, the dextro- (*d*), lævo- (*l*), and inactive (*i*) forms are known.

Some of these stereoisomeric forms are transformed into others simply by the action of pyridine and a little water (*e. g.*, *d*-mannonic acid gives *d*-gluconic acid and *vice versa*), and the inactive forms are resolved into their active constituents by means of the strychnine salts (*see* p. 23).

The **HEPTONIC ACIDS** are also derived from the corresponding sugars, the heptoses (*see later*), *e. g.*, *rhamnohexonic acid*, $C_6H_8(OH)_5 \cdot CO_2H$, from rhamnose; *glucoheptonic acid*, $C_6H_7(OH)_6 \cdot CO_2H$, etc.

D. MONOBASIC ALDEHYDIC ACIDS

(and Aldehydic Alcohols and Dialdehydes)

GLYOXYLIC or **ETHANOLOIC ACID, $CO_2H \cdot CHO + H_2O$,** gives up the molecule of water with which it is combined without decomposing, and may be regarded as having a structure similar to that of chloral hydrate, $CO_2H \cdot CH(OH)_2$; the salts also correspond with this formula, although they retain the aldehydic character. It occurs widespread in nature in sour fruit (gooseberries, etc.), and is obtained synthetically by heating dibromoacetic acid, $CO_2H \cdot CHBr_2$, with water, by reducing oxalic acid electrolytically, or by oxidising ethyl alcohol with nitric acid. It crystallises with difficulty, dissolves in water and distils in steam.

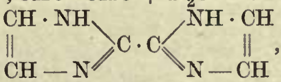
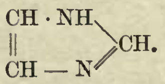
FORMYLACETIC ACID (Semi-aldehyde of Malonic Acid), **$CO_2H \cdot CH_2 \cdot CHO$**, is obtained as acetal from the acetal of acroleïn. The isomeric *β*-hydroxyacrylic acid (*hydroxymethyleneacetic acid*), $CO_2H \cdot CH : CH \cdot OH$, is also known, and is obtained as ester by a synthesis similar to that of ethyl acetoacetate (*see* p. 369). It condenses readily to *trimesic acid*, $C_6H_3(CO_2H)_3$.

GLYCURONIC ACID, $CO_2H \cdot [CH(OH)]_4 \cdot CHO$, is obtained by reducing saccharic acid, and, as lactone, melts at 175°.

GLYCOLLIC ALDEHYDE (Ethanolal), **$OH \cdot CH_2 \cdot CHO$,** is obtained by the action of baryta water on bromoacetaldehyde in the cold. It is known only in aqueous solution and may be regarded as the simplest member of the sugar group, of which it gives all the reactions; it reduces Fehling's solution, even in the cold. When oxidised with bromine water it gives glycollic acid, whilst in presence of dilute alkali it condenses, forming tetrose. If heated in a vacuum, it condenses to a syrup, which retains the reducing character. With phenylhydrazine acetate it yields glyoxal phenylosazone.

GLYCERALDEHYDE, $OH \cdot CH_2 \cdot CH(OH) \cdot CHO$, is obtained together with dihydroxyacetone (as *glycerose*) by oxidising lead glycerate with bromine, or by hydrolysis of its acetal. On condensation, it gives acrose.

ALDOL, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO$ (*see* p. 245), which belongs to this group of compounds, forms a dense oil soluble in water.

GLYOXAL (Ethandial), **$CHO \cdot CHO$,** is the dialdehyde of glycol, and hence combines with 2 mols. of bisulphite $[C_2H_2O_2(SO_3HNa)_2 + H_2O]$ or hydrocyanic acid. It is formed, together with glycollic acid, by gentle oxidation of acetaldehyde with nitric acid. It forms a white mass which is soluble in alcohol or ether and absorbs water with avidity. Even in the cold, alkalis transform it into glycollic acid, $CHO \cdot CHO + H_2O = OH \cdot CH_2 \cdot CO_2H$. With concentrated ammonia, it gives *glycosine*,  , which is converted to a large extent into *glyoxaline* (*iminazole*), .

E. MONOBASIC KETONIC ACIDS

(and Keto-alcohols, Diketones and Keto-aldehydes)

Ketonic acids show all the general reactions of acids—*i. e.*, of the carboxyl group (p. 321)—and of ketones—*i. e.*, of the carbonyl group, CO (p. 243). Their constitution may be deduced from the various syntheses and from the known constitution of the hydroxy-acids derived from them on reduction.

Interesting behaviour is shown by the esters of the *β-ketonic acids*, which, owing to the mobility of a hydrogen atom adjacent to the carbonyl, reacts sometimes in the ketonic form and sometimes in the isomeric *enolic* form, which represents an unsaturated, tertiary alcohol:

$$\underset{\text{Ethyl acetoacetate (keto-form)}}{CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5} \rightleftharpoons \underset{\text{Ethyl hydroxycrotonate (enol-form)}}{CH_3 \cdot C(OH) : CH \cdot CO_2C_2H_5}.$$

The enolic form is stable only as derivatives, *e. g.*, the acetyl-derivatives, $CH_3 \cdot C(O \cdot CO \cdot CH_3) : CH \cdot CO_2C_2H_5$, these derivatives being the more stable the more negative the residues introduced in the direction of the carboxyl.

This phenomenon is *tautomerism* or *pseudoisomerism* (*see* p. 18).

If the *α*-carbon atom, adjacent to the carbonyl, has one of its hydrogen atoms replaced by an alkyl group, thus, $CH_3 \cdot CO \cdot CHR \cdot CO_2C_2H_5$, the phenomenon of tautomerism is still observed, but this ceases to be the case when both these hydrogen atoms are replaced, as in $CH_3 \cdot CO \cdot CR_2 \cdot CO_2C_2H_5$. The mobile hydrogen causing the tautomerism is solely that situate between two carbonyls (1 : 3 diketones):

$$—CO—CH_2—CO— \rightleftharpoons —C(OH) : CH \cdot CO—$$

so that such behaviour is not shown by acetylformic acid, $CH_3 \cdot CO \cdot CO_2H$; diacetyl, $CH_3 \cdot CO \cdot CO \cdot CH_3$; acetonylacetone, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$; levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, etc.

The tautomeric forms may be distinguished and are stable in the crystalline state, even near the melting-point; the reciprocal transformation is continuous and very rapid in either the fused or dissolved state, the two forms finally attaining proportions varying with the conditions (especially temperature and nature of solvent). If separation of the two forms by means of a reagent is attempted, the equilibrium is displaced and the second tautomeric form is transformed into the one which has reacted, so that the mixture behaves as a single substance, unless two reagents are used which act with equal velocities on the two forms giving different, separable compounds; syntheses with ethyl chlorocarbonate appear to correspond with these conditions, which are, however, not easy to obtain.[1]

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[1] Knorr and Kurt Meyer (1911) have succeeded in separating the two components of a tautomeric mixture by cooling to a very low temperature a solution of the mixture in a suitable solvent (*e. g.*, at − 78° the concentrated alcoholic solution of ethyl acetoacetate deposits crystals of the true ketonic form, whereas the enolic isomeride, *i. e.*, ethyl hydroxycrotonate, $CH_3 \cdot C(OH) : CH \cdot CO_2C_2H_5$, remains in solution). Another method of separation consists in cooling to − 78° a suspension of ethyl sodioacetoacetate in methyl ether, adding insufficient HCl to combine with the sodium, filtering the undissolved sodium salt and rapidly evaporating the solution in a vacuum at −78°; the hydroxycrotonic ester remains free from the ketonic compound. The two pure isomerides thus separated may be mixed in different proportions, and comparison of the molecular refractions (*see* p. 18) with that of the ordinary ethyl acetoacetate shows that the latter represents a dynamic equilibrium between 98 per cent. of the ketonic and 2 per cent. of the enolic forms. With this system it is possible to follow the velocity of transformation or the displacement of the equilibrium by the action of a catalyst or of heat. An analogous method serves to resolve tautomeric or pseudomeric mixtures (*see* p. 18) of acetyldibenzoylmethane, $CH_3 \cdot CO \cdot CH(CO \cdot C_6H_5)_2$, tribenzoylmethane, $CH(CO \cdot C_6H_5)_3$, ethyl diacetylsuccinate, $C_2H_5 \cdot CO_2 \cdot CH(CO \cdot CH_3) \cdot CH(CO \cdot CH_3) \cdot CO_2C_2H_5$, and methyl benzoylacetate, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2CH_3$.

On the other hand, Kurt Meyer has determined accurately the percentage of enolic compound present in the tautomeric mixture by titration with bromine, since in solution at 0° the double linking of the enolic form fixes two atoms of bromine in a few seconds, the almost pure

When separated, the two forms may be readily distinguished, since the enol gives an intense coloration with ferric chloride, with which the ketone does not react. After some days, however, the coloration yielded by the former becomes paler, while a colour also appears in the mixture of ketone and ferric chloride, a condition of equilibrium between the two forms being slowly arrived at in each case. Sometimes the enolic form remains unchanged for a long time in chloroform solution, although when dissolved in alcohol it is transformed more or less completely into the ketonic form in the course of a few days.

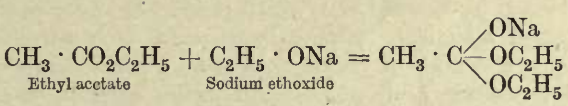
The enolic form—which is soluble in alkali, whereas the ketone is insoluble —*gives* (like *all compounds containing a double bond*) *a greater dispersion and refraction of light*, and also *a greater electromagnetic rotation of the plane of polarisation*,[1] than the corresponding isomerides without double bonds.

METHODS OF PREPARATION. Ketonic acids are formed by gentle oxidation of secondary hydroxy-acids; thus, lactic acid gives pyruvic acid, $CH_3 \cdot CH(OH) \cdot CO_2H + O = H_2O + CH_3 \cdot CO \cdot CO_2H$.

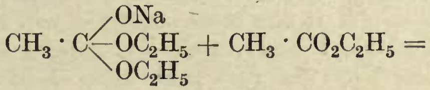
The **α-ketonic acids** are usually obtained by hydrolysing the nitriles, this reaction indicating the constitution :

$$\underset{\text{Acetyl cyanide}}{CH_3 \cdot CO \cdot CN} + 2H_2O = NH_3 + \underset{\text{Pyruvic acid}}{CH_3 \cdot CO \cdot CO_2H}.$$

β-Ketonic acids are obtained as esters by the action of sodium or sodium ethoxide on ethyl acetate or its homologues (*see* the Ethyl Malonate Synthesis, p. 369), thus :



$$\underset{\text{Ethyl acetate}}{CH_3 \cdot CO_2C_2H_5} + \underset{\text{Sodium ethoxide}}{C_2H_5 \cdot ONa} = CH_3 \cdot C\begin{array}{l}\diagup ONa\\ -OC_2H_5\\ \diagdown OC_2H_5\end{array}$$



$$CH_3 \cdot C\begin{array}{l}\diagup ONa\\ -OC_2H_5\\ \diagdown OC_2H_5\end{array} + CH_3 \cdot CO_2C_2H_5 =$$

$$2C_2H_5 \cdot OH + \underset{\text{Ethyl sodioacetoacetate}}{CH_3 \cdot C(ONa) : CH \cdot CO_2C_2H_5}.$$

Acetic acid then readily expels the sodium and liberates *ethyl acetoacetate*, which has not the enolic but the ketonic constitution, $CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5$. The total reaction is hence as follows :

$$CH_3 \cdot CO_2C_2H_5 + CH_3 \cdot CO_2C_2H_5 = C_2H_5 \cdot OH + CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5.$$

Similarly diketones are obtained by the interaction of ethyl acetate and simple ketones in presence of sodium ethoxide :

$$CH_3 \cdot CO_2C_2H_5 + CH_3 \cdot CO \cdot CH_3 = C_2H_5 \cdot OH + CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3.$$

This *ethyl acetate synthesis* has been largely used to prepare compounds of most varied characters. Ethyl formate acts similarly, giving hydroxy-

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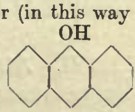
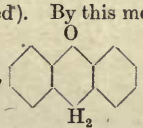
ketonic form being then extractable by means of hexane or petroleum ether (in this way ethyl acetoacetate of 98·5 per cent. purity is extracted). By this means *anthranol*,



, may be separated and distinguished from *anthrone*,



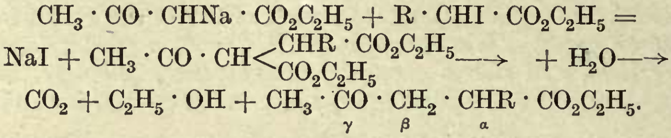
(*see* Aromatic series).

[1] Polarised light passes unchanged through a tube containing an inactive liquid, but if the tube is surrounded by a wire through which an electric current passes, the plane of polarisation is deviated, and, under equal conditions of temperature and current, the deviation is greater for a compound with a double bond than for the isomeride without such a bond.

methylene derivatives [containing the group $—C(OH) =$], which are isomeric with the keto-aldehydes :

$$\underset{\text{Acetone}}{CH_3\cdot CO\cdot CH_3} + \underset{\text{Ethyl formate}}{H\cdot CO_2C_2H_5} = C_2H_5\cdot OH + \underset{\text{Hydroxymethyleneacetone}}{OH\cdot CH : CH\cdot CO\cdot CH_3}.$$

γ-Ketonic acids are obtained by the ketonic decomposition (*see later*) of the products of reaction of ethyl sodioacetoacetate with esters of α-halogenated acids :



$$CH_3\cdot CO\cdot CHNa\cdot CO_2C_2H_5 + R\cdot CHI\cdot CO_2C_2H_5 =$$
$$NaI + CH_3\cdot CO\cdot CH{<}\begin{matrix}CHR\cdot CO_2C_2H_5\\ CO_2C_2H_5\end{matrix}\longrightarrow \; + H_2O\longrightarrow$$
$$CO_2 + C_2H_5\cdot OH + CH_3\cdot \underset{\gamma}{CO}\cdot \underset{\beta}{CH_2}\cdot \underset{\alpha}{CHR}\cdot CO_2C_2H_5.$$

Properties of Ketonic Acids. While the α- and γ-ketonic acids are stable, the β-acids readily lose CO_2, giving the corresponding ketones. Reduction of γ-ketonic acids yields, not hydroxy-acids, but γ-lactones.

As we saw was the case with malonic acid (*see* p. 369), the esters of β-ketonic acids contain a hydrogen atom readily replaceable by metals, *e. g.*, ethyl *sodioacetoacetate*, $CH_3\cdot CO\cdot CHNa\cdot CO_2C_2H_5$.

Further, ketonic acids readily form condensation products; with aniline they give quinolines; with phenylhydrazine, pyrazoles, etc.

PYRUVIC ACID, $CH_3\cdot CO\cdot CO_2H$, is obtained by the dry distillation of tartaric or racemic acid, an intermediate product in the reaction being possibly glyceric acid (formed by loss of CO_2), which then loses water and yields pyruvic acid. It is formed also by oxidising lactic acid with permanganate or by hydrolysing acetyl cyanide. Pyruvic acid is a liquid with an odour of acetic acid and of meat-extract, and is soluble in water, alcohol, or ether. It boils at 165° and solidifies at 9°. It is a more energetic acid than propionic owing to the presence of a carbonyl group in close proximity to the carboxyl. Its constitution is indicated by the fact that with nascent hydrogen it gives ethylidenelactic acid. It readily forms condensation products (*e. g.*, benzenes; and with ammonia, pyridine compounds). When heated at 150° with dilute sulphuric acid, it loses CO_2, forming acetaldehyde. Electrolysis of a concentrated solution of potassium pyruvate results in the union of the anion of the acid, $CH_3\cdot CO\cdot COO'$ with the ion OH', cyanogen and acetic acid being formed; at the same time two anions combine with loss of $2CO_2$ and formation of *diacetyl*, $CH_3\cdot CO\cdot CO\cdot CH_3$. This represents the general behaviour of potassium salts of ketonic acids on hydrolysis.

Of interest is its conversion into ethyl alcohol and also into acetaldehyde and CO_2 by enzyme action (*see* Note, p. 136).

Of the derivatives, *cysteine* (α-amino-β-thiolactic acid), $SH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, and *cystine*, the corresponding disulphide, may be mentioned.

α-Ketobutyric acid, $CH_3\cdot CH_2\cdot CO\cdot CO_2H$, has no special importance.

ACETOACETIC ACID (β-Ketobutyric acid), $CH_3\cdot CO\cdot CH_2\cdot CO_2H$, is obtained in the free state by cautious hydrolysis of its ester, and forms an extremely acid liquid soluble in water, in which it gives a red coloration with ferric chloride; when heated, it readily loses CO_2 with production of acetone.

ETHYL ACETOACETATE, $CH_3\cdot CO\cdot CH_2\cdot CO_2C_2H_5$, is of far greater importance than the free acid, owing to the very varied syntheses in which it finds application. This ester is obtained in the form of its crystalline sodium derivative by the action of sodium and alcohol (sodium ethoxide) on ethyl acetate (*see above*).

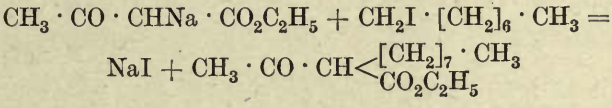
Ethyl acetoacetate (freed from sodium by means of acetic acid) is a liquid having a pleasant, fruity odour, and dissolves readily in alcohol or ether and slightly in water, in which it gives a red coloration with ferric chloride. It has a neutral reaction and the sp. gr. 1·030; it boils at 181° and is found in diabetic urine. When boiled with dilute alkali or dilute sulphuric acid, it undergoes *ketonic decomposition*, forming CO_2, acetone and alcohol:

$$CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + H_2O = CO_2 + C_2H_5 \cdot OH + CH_3 \cdot CO \cdot CH_3.$$

With concentrated alcoholic potassium hydroxide, it undergoes *acid decomposition*, producing 2 mols. of acetic acid:

$$CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + 2H_2O = C_2H_5 \cdot OH + 2CH_3 \cdot CO_2H.$$

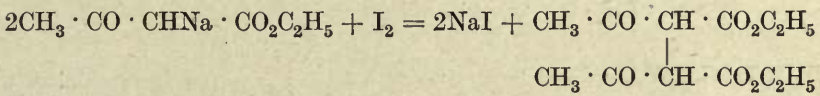
Its great reactivity is due to the readiness with which one of the hydrogen atoms is replaceable by metals (Ba, Al, Zn, Ag, Cu, etc., in ammoniacal solution), especially by sodium. *Ethyl sodioacetoacetate*, $CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5$, is a white solid soluble in water, while ethyl acetoacetate is soluble in alkali, from which it is reprecipitated by acids. The sodium is readily replaced by different alkyl groups by the action of the corresponding alkyl iodides (*see* the analogous syntheses with Ethyl Malonate, p. 369). Since the compounds thus obtained can be subjected to either acid or ketonic decomposition, it will readily be seen how very varied acids and ketones may be obtained by means of ethyl acetoacetate. For instance, the action of normal octyl iodide on ethyl sodioacetoacetate yields *methyl nonyl ketone*, a constituent of oil of rue:



$$CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5 + CH_2I \cdot [CH_2]_6 \cdot CH_3 =$$
$$NaI + CH_3 \cdot CO \cdot CH{<}\begin{matrix}[CH_2]_7 \cdot CH_3 \\ CO_2C_2H_5\end{matrix}$$

this compound, by ketonic decomposition, giving *methyl nonyl ketone*, which must hence have the normal structure, $CH_3 \cdot CO \cdot CH_2 \cdot [CH_2]_7 \cdot CH_3$.

Further, by eliminating the sodium from ethyl sodioacetoacetate by means of iodine, the two residues combine, forming *ethyl diacetylsuccinate:*



$$2CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5 + I_2 = 2NaI + \begin{matrix}CH_3 \cdot CO \cdot CH \cdot CO_2C_2H_5 \\ | \\ CH_3 \cdot CO \cdot CH \cdot CO_2C_2H_5\end{matrix}$$

and this ester, on ketonic decomposition (boiling with 20 per cent. potassium carbonate solution), reacts with $2H_2O$ and gives $2CO_2$, $2C_2H_5 \cdot OH$ and *acetonylacetone*, $CH_3 \cdot \underset{4}{CO} \cdot \underset{3}{CH_2} \cdot \underset{2}{CH_2} \cdot \underset{1}{CO} \cdot CH_3$, which has a normal carbon-atom chain and is a 1 : 4 diketone.

Ethyl acetoacetate also combines with formaldehyde (in presence of diethylamine), with acetone and with ammonia; with aniline it gives diphenylcarbamide. With one or two mols. of sulphuryl chloride it gives *ethyl chloracetoacetate* (b.-pt. 194°, sp. gr. 1·19 at 14°) or *ethyl dichloracetoacetate*, $CH_3 \cdot CO \cdot CCl_2 \cdot CO_2C_2H_5$, which boils at 206° and has the sp. gr. 1·293 at 16°.

LEVULINIC ACID, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, is obtained synthetically by the acid decomposition of the product of reaction of ethyl acetoacetate and ethyl chloracetate. It may be prepared by boiling hexoses, cane-sugar, cellulose, gum, starch, etc., with concentrated hydrochloric acid.

It melts at 33° and boils at 239° with slight decomposition, or at 144° under 12 mm. pressure.

It is sometimes used in the printing of textiles.

KETO-ALCOHOLS

ACETONEALCOHOL or **ACETYLCARBINOL** (Propanolone), $CH_3 \cdot CO \cdot CH_2 \cdot OH$, is formed by heating either grape-sugar with fused potassium hydroxide or a mono-halogenated acetone with barium carbonate. It is a liquid which boils almost unchanged at 147° and reduces Fehling's solution even in the cold.

DIHYDROXYACETONE or **GLYCEROSE**, $OH\cdot CH_2\cdot CO.CH_2\cdot OH$, is formed together with glyceraldehyde by oxidising glycerol with nitric acid. It has a sweet taste and may indeed be regarded as a triose sugar. It crystallises in colourless plates and reduces Fehling's solution in the cold.

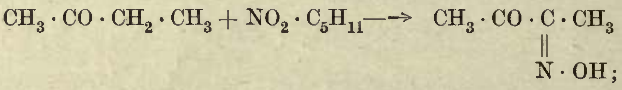
BUTAN-2-OL-3-ONE (Dimethylacetol), $CH_3\cdot CO\cdot CH(OH)\cdot CH_3$, also reduces Fehling's solution and is obtained by reducing diacetyl. It is a liquid soluble in water and boils at 142°.

The higher homologue, *acetoisopropyl alcohol*, $CH_3\cdot CO\cdot CH_2\cdot CH(OH)\cdot CH_3$, b.-pt. 177°, is also known and is formed by the condensation (by means of alkali) of aldehyde with acetone. Removal of water from this compound yields **Ethylideneacetone**, $CH_3\cdot CO\cdot CH:CH\cdot CH_3$, boiling at 122°.

DIKETONES

All diketones give mono- and di-oximes, and mono- and di-hydrazones, the latter (as with the aldehydes) bearing the name of *osazones* and being usually yellow. They often exhibit tautomerism and give rise to various cyclic condensation products.

DIACETYL or **α-DIKETOBUTANE** (Butandione), $CH_3\cdot CO\cdot CO\cdot CH_3$, is prepared by the general method for diketones, namely, by treating methyl ethyl ketone, $CH_3\cdot CO\cdot C_2H_5$, with amyl nitrite and a little HCl, the CH_2 group being transformed into — C : NOH, giving an *isonitrosoketone*, thus :

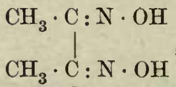


$$CH_3\cdot CO\cdot CH_2\cdot CH_3 + NO_2\cdot C_5H_{11} \longrightarrow CH_3\cdot CO\cdot \underset{\underset{N\cdot OH}{\|}}{C}\cdot CH_3;$$

when boiled with dilute sulphuric acid, this compound loses the hydroxyiminic group (as hydroxylamine), the diketone remaining.

It is a yellow liquid which has a penetrating odour, dissolves in water and boils at 88°, giving yellowish-green vapour (sp. gr. 0·973 at 20°). With hydrogen peroxide, diacetyl is converted quantitatively into 2 mols. of acetic acid :

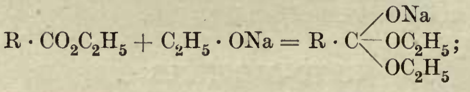
$$CH_3\cdot CO\cdot CO\cdot CH_3 + H_2O_2 = 2CH_3\cdot CO_2H.$$

DIMETHYLGLYOXIME (Diacetyldioxime),  $\begin{array}{l} CH_3\cdot C:N\cdot OH \\ \quad | \\ CH_3\cdot C:N\cdot OH \end{array}$, forms shining, white crystals, m.-pt. 234·5°, insoluble in water, but soluble in alcohol or ether. It is obtained by shaking 50 grams of methyl acetoacetate in the cold with a solution of 30 grams of NaOH in 750 grams of water, allowing to stand for twelve hours, and adding 25 grams of sodium nitrite and a little methyl orange; to the mass, cooled with ice, 30 per cent. sulphuric acid is gradually added until the yellow coloration changes to reddish. Three hours later an aqueous solution of 25 grams of hydroxylamine hydrochloride is added, and sufficient soda crystals to render the reaction alkaline. The dimethylglyoxime crystals separating are collected on a suction-filter, washed with water and dried (yield 55 per cent. of the ester used).

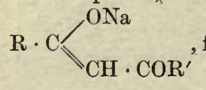
Dimethylglyoxime is the most sensitive reagent for *ferrous salts*, but is now used more especially for the quantitative separation of nickel from cobalt, since in neutral or ammoniacal solution a 1 per cent. alcoholic solution of the oxime precipitates nickel, but not cobalt or other metals.

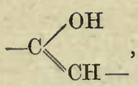
Prior to the war it cost £5 4*s*. per kilo.

ACETYLACETONE, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$. The best general method for preparing 1 : 3-diketones consists in treating an ester with sodium ethoxide :



$$R\cdot CO_2C_2H_5 + C_2H_5\cdot ONa = R\cdot C\begin{array}{l} \diagup ONa \\ - OC_2H_5 \\ \diagdown OC_2H_5 \end{array};$$

this compound, when treated with a ketone, $R'\cdot CO\cdot CH_3$, loses 2 mols. of alcohol and yields  $R\cdot C\begin{array}{l} \diagup ONa \\ \diagdown CH\cdot COR' \end{array}$, from which the sodium is expelled by a dilute acid. This enolic form,



$-C\begin{smallmatrix}\diagup OH \\ \diagdown CH-\end{smallmatrix}$, readily passes into the ketonic form, $-CO-CH_2-$, thus giving the compound $R \cdot CO \cdot CH_2 \cdot CO \cdot R'$.

Another general method for obtaining 1 : 3-diketones consists in treating the sodium derivatives of acetylene homologues with an acid chloride and then acting on the acetylenic product with sulphuric acid, so that it combines with water:

$$\underset{\text{Amylacetylene}}{CH_3 \cdot [CH_2]_4 \cdot C \vdots CNa} + \underset{\text{Acetyl chloride}}{CH_3 \cdot CO \cdot Cl} = NaCl + CH_3 \cdot [CH_2]_4 \cdot C \vdots C \cdot CO \cdot CH_3;$$

the latter $+ H_2O \longrightarrow CH_3 \cdot [CH_2]_4 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$.

As in ethyl acetoacetate and ethyl malonate, the two hydrogen atoms of the methylene group between the two carbonyl groups are here also replaceable by metals, giving volatile compounds which are soluble in chloroform, benzene, etc., and differ from true salts, their solutions exhibiting very slight electrical conductivity.

Acetylacetone has a pleasant odour and boils at 137°. When boiled with water it yields acetone and acetic acid.

ACETONYLACETONE (γ-Diketohexane or Hexa-2 : 5-dione), $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$, is obtained by ketonic decomposition of the product of interaction of ethyl acetoacetate and ethyl chloracetate (*see also* Levulinic Acid); it boils at 194° and has an agreeable smell.

KETO-ALDEHYDES AND HYDROXYMETHYLENEKETONES

PYRUVIC ALDEHYDE (Methylglyoxal or Propanolone), $CH_3 \cdot CO \cdot CHO$, is a volatile oil obtained by decomposing its oxime (isonitrosoacetone) with dilute acid (*see* Diacetyl).

ACETOACETALDEHYDE, $CH_3 \cdot CO \cdot CH_2 \cdot CHO$, was formerly thought to have been obtained in the free state, but more exact study has now shown the compound in question to be the unsaturated isomeride, **HYDROXYMETHYLENEACETONE**, $CH_3 \cdot CO \cdot CH : CH \cdot OH$, which has an acid character and is obtained by the interaction of acetone and ethyl formate in presence of sodium ethoxide (*see* Ethyl Acetoacetate). It boils at 100° and readily condenses into 1 : 3 : 5-triacetylbenzene, $C_6H_3(CO \cdot CH_3)_3$.

LEVULINALDEHYDE (Pentanal-4-one), $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$, boils at 187°. It is obtained as a decomposition product of the ozonide of rubber (*q. v.*).

F. POLYVALENT DIBASIC HYDROXY-ACIDS AND THEIR DERIVATIVES

TARTRONIC ACID (Hydroxymalonic or Propanoldioic Acid), $CO_2H \cdot CH(OH) \cdot CO_2H$, is formed by the spontaneous decomposition of nitrotartaric acid and is obtained synthetically by oxidising glycerol with potassium permanganate, by eliminating bromine from bromomalonic acid by the action of moist silver oxide, or by reducing Mesoxalic Acid, $CO(CO_2H)_2$. It crystallises with $\frac{1}{2}H_2O$ and melts at 184°, losing CO_2 and forming polyglycollides. It is soluble in water, alcohol, or ether.

MALIC ACID (Hydroxysuccinic or Butanoldioic Acid), $CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, occurs in abundance in unripe fruits (apples, grapes, quinces, and sorb-apples, from which it is extracted). Its crystals melt at 100° and it dissolves in water or alcohol and, to a slight extent, in ether. When subjected to dry distillation, it gives fumaric acid and maleic anhydride. Synthetically it is obtained from maleic or fumaric acid or asparagine, and also by the action of moist silver oxide on bromosuccinic acid, and by the reduction of tartaric acid by means of hydriodic acid.

As it contains an asymmetric carbon atom, malic acid forms three optically different stereoisomerides, all of which are known. Natural malic acid is lævo-rotatory, that derived from *d*-tartaric acid dextro-rotatory, and that obtained by other syntheses inactive but resolvable into active components by fractional crystallisation of the cinchonine salt.

It gives an acid calcium salt readily soluble, and a normal salt slightly soluble in water. The presence of the alcoholic group is proved by the formation of acetylmalic acid (*see* p. 224).

For the amido-derivatives, asparagine, etc., *see later.*

Of the *higher homologues of malic acid*, the following are known: Four isomeric acids, $C_3H_5(OH)(CO_2H)_2$ (*α*- and *β-hydroxyglutaric acids, itamalic* and *citramalic acids*); diaterebinic acid, $C_5H_9(OH)(CO_2H)_2$, which readily forms a lactone, and terebinic acid, $C_7H_{10}O_4$.

TARTARIC ACIDS, $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$

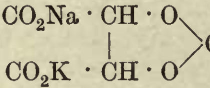
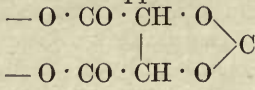
These are dibasic and tetravalent, as they contain two secondary-alcoholic groups. The presence of two asymmetric carbon atoms leads to the existence of four stereoisomerides, which have already been considered on pp. 20–21: (1) ordinary or *d*-tartaric acid; (2) *l*-tartaric acid; (3) racemic or para- or di-tartaric acid; (4) i- or meso- or anti-tartaric acid.

They are obtained synthetically from dibromosuccinic acid, $CO_2H \cdot CHBr \cdot CHBr \cdot CO_2H$, and moist silver oxide, from glyoxal cyanohydrin, from glyoxylic acid by reduction, from mannitol by oxidation with nitric acid, and from fumaric or maleic acid by oxidation.

(1) **d-TARTARIC ACID.** This is the ordinary tartaric acid, which occurs abundantly as such, and as monopotassium tartrate (tartar) in many fruits —especially in the grape, and hence in wine, from which it is extracted in a manner to be described.

Dextro-rotatory tartaric acid forms hemimorphic, monoclinic prisms with a decided and pleasant acid taste. It is readily soluble in water or alcohol and almost insoluble in ether. One hundred parts of water dissolve 114 parts of the acid at 0°, 125·7 at 10°, 139·4 at 20°, 156·2 at 30°, 176 at 40°, 195 at 50°, 217·5 at 60°, 243·6 at 70°, 273·3 at 80°, 306·5 at 90°, and 343·3 at 100°. The acid melts at 170°, giving rise to various anhydrides and to pyruvic and pyrotartaric acids; ultimately it carbonises with an odour of burnt bread or, if the temperature is raised considerably, of burnt sugar.

Energetic oxidising agents convert it into tartronic acid or dihydroxytartaric acid and finally into formic acid, carbon dioxide, etc. In the hot, it reduces ammoniacal silver solutions (*see* p. 413 for a sensitive reaction for tartaric acid). Certain bacteria transform it into succinic acid. When burned, tartaric acid and tartrates emit an odour of burnt bread, thus differing from citric acid and citrates, which give a pungent odour. Even in the hot, it resists the action of sulphuric acid of 62° Bé.

Owing to the presence of alcoholic groups, tartaric acid, like glycerol, hinders the precipitation by alkali of many metallic oxides, *e. g.*, of cupric oxide in *Fehling's solution* (containing caustic soda, copper sulphate, and sodium potassium tartrate; *see* Sugar Analysis), the intensely blue, soluble compound,  $\left.\begin{array}{l}CO_2Na \cdot CH \cdot O \\ \qquad\quad | \\ CO_2K \cdot CH \cdot O\end{array}\right\rangle Cu$, being formed; this compound is not precipitable by alkalis, since the copper no longer functions as cation, but is contained in the anion,  $\left.\begin{array}{l}-O \cdot CO \cdot CH \cdot O \\ \qquad\qquad\quad | \\ -O \cdot CO \cdot CH \cdot O\end{array}\right\rangle Cu$, which migrates to the positive pole or anode when the salt is electrolysed.

Tartaric acid is used in dyeing, in the wine industry, in the preparation of aerated beverages (lemonade), in medicine, etc.

The following salts of tartaric acid may be mentioned, acid potassium tartrate being considered more in detail later.

ACID POTASSIUM TARTRATE (Cream of Tartar), $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2K$, is slightly soluble in water or in dilute alcohol, and has a pleasant acid taste. For its commercial preparation, *see* Tartar Industry.

NORMAL POTASSIUM TARTRATE, $C_4H_4O_6H_2 + \frac{1}{2}H_2O$, is readily soluble in water and separates from highly concentrated solutions in monoclinic prisms. One hundred grams dissolves in 75 grams of water at 2°, in 66 grams at 14°, in 63 grams at 23°, or in 47 grams at 64°.

SODIUM POTASSIUM TARTRATE (Rochelle Salt), $C_4H_4O_6NaK + 4H_2O$, is prepared by neutralising cream of tartar solution with sodium carbonate. Copper and iron, present as impurities, are removed by means of hydrogen sulphide, the solution being then heated with good animal charcoal, filtered, concentrated and allowed to crystallise; the Rochelle salt separates in thick columns readily soluble in water and slightly so in alcohol. One hundred grams of the crystallised salt dissolves in 170 grams of water at 6°. It is used to reduce silver salts in the silvering of mirrors and also for medicinal purposes and to prepare Fehling's solution. It costs about 72*s*. per cwt.

CALCIUM TARTRATE, $C_4H_4O_6Ca + 4H_2O$, occurs ready formed in the grape and in senna leaves. The crystallised salt (1 part) dissolves in 352 parts of boiling water or in 6265 parts at 15°. It is readily soluble in cold sodium hydroxide solution, from which it separates in the hot as a white jelly, to be redissolved on cooling. It dissolves in acetic acid, thus differing from calcium oxalate. It is soluble also in alkali tartrates and in ammonium salts. The crystalline tartrate loses part of its water of crystallisation at 60°, 15 per cent. at 110°, and the whole at 130°.

TARTAR EMETIC (or Potassium Antimonyl Tartrate), $C_4H_4O_6(SbO)K + \frac{1}{2}H_2O$, is prepared by precipitating SbOCl from a solution of $SbCl_3$ by means of water, boiling the precipitate with soda solution and dissolving the Sb_2O_3 thus formed in a solution of four or five times its weight of potassium hydrogen tartrate in 50 parts of water. After filtration and concentration the solution deposits, on cooling, efflorescent, trimetric pyramids, which are soluble in water (1 : 13 at 20°, 1 : 6 at 50°) but insoluble in alcohol. At 100° it loses its water of crystallisation and at 220° the double molecule loses water of constitution and gives $2KSbC_4H_2O_6$. It is poisonous and is used in medicine as an emetic and in dyeing cotton as a mordant for basic dyes (price about £4 16*s*. per cwt.). Germany imported 202 tons in 1908 and 391 in 1909, the respective exports being 1030 and 1090 tons in the two years.

(2) ***l*-TARTARIC ACID** differs from the *d*-acid only in the opposite sign of its rotation and in the opposed hemihedry of its crystals. Mixing of the concentrated aqueous solutions of the two acids results in development of heat and the formation of inactive tartaric acid.

(3) **RACEMIC ACID** (Paratartaric Acid), $(C_4H_6O_6)_2 + 2H_2O$, represents a mixture of dextro- and lævo-tartaric acids in equal proportions, and is hence optically inactive (*see* p. 21). When heated alone or, better, in presence of concentrated caustic soda solution, either the *d*-acid or the meso-acid (*see later*) is transformed into racemic acid. The latter is obtained from the mother-liquors of ordinary *d*-tartaric acid. The molecular weight, determined cryoscopically or from the vapour densities of the esters, corresponds with the simple molecule, $C_4H_6O_6$. It forms triclinic crystals which effloresce in the air, and is less soluble than the active acids. From *sodium ammonium racemate* crystals, $(C_4H_4O_6)_2Na_2(NH_4)_2 + 2H_2O$; Pasteur separated those showing dextro- from those showing lævo-hemihedry, thus resolving racemic acid into its optically active constituents. Only in the crystalline state is the molecule of racemic acid regarded as double that of tartaric acid, whilst in dilute aqueous solution it is assumed to be decomposed completely into the two optical antipodes.

(4) **MESOTARTARIC ACID**, $C_4H_6O_6 + H_2O$, is optically inactive (p. 21) and is not merely a mixture of the active compounds. It is obtained by prolonged boiling of *d*-tartaric acid with excess of caustic soda. Its potassium salt is more soluble in water than those of the other tartaric acids.

THE TARTAR INDUSTRY

MANUFACTURE OF POTASSIUM BITARTRATE (Cream of Tartar or Potassium Hydrogen Tartrate). Although the crude prime material of this industry is very abundant in Italy in wine residues, it is only within the last few years that the working has been placed on a rational basis, the tartar being refined and tartaric acid prepared. Although these prime materials are subject to an export duty (10½*d.* per cwt.), the exportation from Italy amounted to about 17,800 tons, worth £480,000, in 1905, and 17,850 tons, worth £416,000, in 1910. The treatment of these products requires, besides special technical ability, also considerable quantities of fuel, and to this are partly due the difficulties of the Italian manufacturers.

Cream of tartar occurs abundantly in the green extremities of vine-shoots and in the grape, and part of it remains in the pressed *vinasse.* The vinasse of southern grapes contains as much as 4 per cent. of cream of tartar, and that of other grapes from 2 to 2·5 per cent. Vinasse that has not been in contact with the fermenting must, and that of second wines have practically no commercial value.[1]

Another portion of the cream of tartar which remains dissolved in the must gradually separates (*lees*) as fermentation proceeds—cream of tartar being less soluble in alcoholic liquids (wine)—and finally part of it is deposited as a crystalline crust on the walls of the casks during the winter, the solubility being less in the cold.

The following table shows, for various temperatures : I, the number of grams of cream of tartar dissolved by 100 grams of water ; II, the number of grams dissolved by 100 grams of 10 per cent. aqueous alcohol solution ; and III, the number of grams contained in 100 c.c. of the saturated solution.

	0°	5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°	90°	100°
I.	0·320	0·360	0·400	0·470	0·570	0·680	0·900	1·31	1·81	2·40	3·20	4·50	5·70	6·90
II.	0·141	0·175	0·212	0·253	0·305	0·372	0·460	0·570	0·710	—	—	—	—	—
III.	0·370	—	0·376	0·411	—	0·843	1·020	1·450	1·931	2·475	3·160	4·050	—	5·850

Alcoholic potassium acetate solution transforms cream of tartar partly into the normal tartrate, whilst the presence of free acetic acid hinders such transformation.

Tartaric acid causes a slight diminution in the solubility of tartar in wine, whereas mineral acids increase this solubility.

These crude products are of different colours according as they are obtained from white wines (white tartar) or red wines (red tartar), and according to the degree of purity.

Fresh *wine lees* (forming about 5 per cent. of the wine) are slimy, of a dirty red colour, and contain yeasts, colouring-matters, cream of tartar (10 to 25 per cent.), and calcium tartrate (6 to 20 per cent.). Italian wine lees are the richest in potassium bitartrate and the poorest in calcium tartrate. When removed from the vats, the lees are placed to drain in strong bags suspended by cords, the bags being afterwards tied up and pressed slightly in a press. They are then removed from the bags and dried in the air, being turned from time to time. When pressed and almost dry, they contain more than double as much tartar as when in the fresh state (about 10 per cent. of moisture, 6 to 10 per cent. of lime, 3 to 5 per cent. of sand, 25 to 40 per cent. of tartaric acid). In some large wineries

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[1] One quintal of grapes yields 30 to 35 kilos of vinasse and 65 to 70 of must, so that the annual Italian production of 40,000,000 quintals would correspond with 15 to 20 million quintals of vinasse, containing, on the average, more than 3 per cent. of tartar, *i. e.*, a total of about 700,000 quintals (70,000 tons) of tartar. The vinasse distilled in Italy in 1909 amounted to 368,000 tons, which should have yielded 11,000 tons of cream of tartar, but this was largely lost. The tartar is estimated by the method of Carles : a kilo of the vinasse is chopped and mixed, and 100 grams weighed and boiled for ten minutes with 700 c.c. of water in a litre flask, the liquid being subsequently made up to the mark with distilled water. Five hundred cubic centimetres of the filtered solution is concentrated to about 100 c.c., 70 c.c. of saturated calcium acetate solution being then added to the boiling liquid ; after mixing, the liquid is allowed to cool for twelve hours, the precipitated calcium tartrate being then collected on a tared filter, washed with water, dried at 60°, and weighed. Multiplication of the result by 2 and deduction of 5 per cent. (to allow for the volume occupied by the vinasse in the litre flask) gives the calcium tartrate per 100 grams of vinasse ; further multiplication by 0·723 gives the corresponding amount of potassium hydrogen tartrate. Ciapetti has rendered this method more exact by transforming the calcium tartrate (by potassium bioxalate in the hot) into potassium hydrogen tartrate, filtering and washing the residue, concentrating the filtrate and adding alcohol to precipitate the potassium bitartrate ; the latter is washed, redissolved in hot water and titrated with decinormal caustic soda solution (*see below,* Analysis of Tartar).

the lees are passed directly to the filter-presses, cakes which are readily dried being thus obtained.

The crude tartar contains 45 to 70 per cent. of potassium bitartrate and calcium tartrate, and, if washed and crystallised once from hot water, this content may increase to 75 to 87 per cent.,[1] the product being then placed on the market under the name of *crystals.*

As a rule 60 to 70 per cent. of the total tartar is extracted from the vinasse after the alcohol has been distilled off with steam in the manner indicated on p. 170. The forms of apparatus there shown give almost saturated, boiling solutions of tartar (the remaining vinasse being centrifuged or pressed to remove all the tartaric liquors), which are allowed to cool in shallow, wooden vessels. In these vessels are hung, after some time, strings

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[1] **Analysis of Tartar.** Tartar being a rather expensive substance (£3 to £4 per cwt.), it is frequently adulterated with sand, gypsum, etc. It is always bought and sold on its strength, the potassium bitartrate or the total tartaric acid (thus including both the calcium tartrate and the free tartaric acid) being determined.

A homogeneous sample is finely ground and sieved, the residue being again ground.

A test which is not very exact, but is rapid and largely used, is the *direct titration test.* The coarse *impurities,* sand, clay, sulphur, woody matter, yeasts, etc., are estimated by boiling a known weight of the crude tartrate with water acidified with HCl, and collecting, washing, drying, and weighing the residue on a tared filter; the residue is sometimes ashed.

The calcium carbonate is determined by treating with an acid in the calcimeter and measuring the carbon dioxide evolved, and the total lime, including that of the tartrate, by calcining a given weight of the tartar, dissolving out the potassium carbonate, treating the residual calcium carbonate with excess of standard nitrous acid solution, and measuring the excess of the acid by titration with soda solution. The *total lime* is, however, best estimated by dissolving 2 grams in HCl, neutralising with ammonia, precipitating with ammonium oxalate, and heating on a water-bath, the precipitate being subsequently collected on a filter, ignited in a platinum crucible and weighed as CaO.

The *titration test* of the quantity of acid potassium tartrate is carried out by dissolving a weighed amount (2 to 3 grams) of the tartar in water and titrating the boiling solution with N/4-sodium hydroxide solution, using very sensitive litmus paper as indicator; 1 c.c. of N/4-caustic soda solution corresponds with 0·047 gram of potassium bitartrate. Multiplication of the amount of bitartrate by 0·798 yields the corresponding amount of tartaric acid.

For international trade, the potassium bitartrate is nowadays estimated by the *filtration process,* which largely excludes errors due to the presence of tannin substances and other impurities which also react with litmus :

2·35 grams of the substance (crude tartar, sludge or lees) are heated to boiling for five minutes with 400 c.c. of water in a 500 c.c. flask; water is again added and the whole cooled, made up to 500 c.c., mixed and filtered through a folded filter. Of the filtrate 250 c.c. are heated to boiling and titrated with N/4-potassium hydroxide solution (standardised with pure bitartrate), sensitive litmus paper being used as indicator.

For more exact determinations, *Kämmer's recrystallisation method* is employed :

4·7025 grams of substance (molecular weight of tartar divided by 40) are heated to boiling with 30 to 40 c.c. of water in a 100 c.c. flask, the solution being then neutralised with N/4-caustic soda, of which 1 to 2 c.c. in excess are added. The volume is made up to 100 c.c. and of the filtered solution, 20 c.c. are rendered decidedly acid with acetic acid and treated with 100 c.c. of a mixture of alcohol and ether, which separates the potassium bitartrate completely in crystals. These are collected on a filter, washed with alcohol and ether, redissolved in boiling water, and titrated with N/20-soda solution.

Determination of the total tartaric acid. This gives the total content of potassium bitartrate, calcium tartrate, and free tartaric acid. The Goldenberg-Geromont hydrochloric acid process, which was formulated as follows at the Congress of Applied Chemistry at Turin in 1902, is generally used :

Six grams of the substance are treated for eight to ten minutes in a small beaker with 9 c.c. (for products poor in tartar) or 18 c.c. (for richer products) of cold HCl (sp. gr. 1·10), the whole being then washed into a 100 c.c. flask, made up to volume, mixed, and passed through a dry pleated filter. Fifty cubic centimetres of the filtrate are *boiled* for ten to fifteen minutes in a tall 250 to 300 c.c. beaker with 5 (or 10) c.c. of concentrated potassium carbonate solution (66 grams in 100 c.c. of water), the liquid being then washed into a 100 c.c flask, cooled, made up to volume, and filtered through a pleated filter. Fifty cubic centimetres of this filtrate are taken to dryness in a half-litre dish, redissolved in 5 c.c. of boiling water, and vigorously stirred with 4 to 5 c.c. of glacial acetic acid; when the liquid is cold, 100 to 110 c.c. of 96 per cent. alcohol are mixed in, and the potassium bitartrate allowed to deposit. This is filtered under pressure, the dish, rod, and filter being repeatedly washed with alcohol. The filter and the bitartrate are then washed into the same dish with boiling water, with which the volume is made up to about 300 c.c. The liquid is then boiled and titrated with N/4-alkali, the end-point being determined with sensitive litmus paper.

To eliminate the error due to the volume occupied by the impurities in the original flask, 0·7 per cent. is deducted from the total content in the case of low-grade tartars (containing less than 20 per cent. of bitartrate) and $0{\cdot}7 - (n \times 0{\cdot}02)$ in the case of those containing 20 to 50 per cent., n being the excess percentage over 20; beyond 50 per cent. the correction becomes almost zero.

studded with tartar crystals, on which less impure crystals gradually form. The deposit forming on the walls of the vessels is of a less degree of purity, and that on the bottom contains many coloured impurities. In five to six days the crystallisation is complete, more rapid and complete separation being attained in very cold places or by the use of artificial cooling. The mother-liquors decanted from the tartar may be utilised again for extraction of vinasse, but when they become too rich in impurities or mucilaginous substances, they are either used as fertilisers, since they contain potassium salts, or, better, are treated (Carles, 1910) at boiling temperature with 60 grams of potassium ferrocyanide per hectolitre, the iron, alumina, copper, etc., present being thus removed; the clarified liquid is treated with lime to separate calcium tartrate, the potassium salts being recoverable from the filtered solution by the Alberti process (*see later*).[1] The dregs deposited during the extraction of the cream of tartar from the vinasse contain, in the dry state, 30 to 60 per cent. of potassium bitartrate and 10 to 20 per cent. of calcium tartrate.

The *refining* of crude tartar from vinasse, lees, etc., is very difficult with the poorer products, and in practice rich and poor materials are often mixed so as to give a content of 60 to 65 per cent. when a highly refined tartar is not required.

The crude tartar or other mixture should first be ground and then sieved to remove pieces of wood and other impurities. In order to destroy certain impurities and protein substances and hence hasten the filtration of the subsequent aqueous solutions, the lees or low-quality tartar is treated with concentrated sulphuric acid (60° Bé.) or heated in revolving iron cylinders until the temperature reaches 160° to 180°, the loss in weight being 8 to 12 per cent. (water together with 2 to 3 per cent. of cream of tartar). It is then introduced into a perforated copper cylinder placed almost on the bottom of a large wooden vessel furnished with copper or aluminium steam coils. Care is taken not to use an excess of water, which would involve waste of fuel, and generally 6 to 8 parts of water are taken per 1 part of tartar. A hood is usually fitted over the vessel to carry off the steam from the boiling solution. In order to transform the calcium tartrate present into potassium bitartrate, 3 kilos of hydrochloric acid (20 Bé.), and 3 kilos of potassium sulphate (previously dissolved in 20 litres of water) are added to the water per kilo of lime (CaO) contained in the calcium tartrate (*see* method of determination given above). The liquid is stirred occasionally, boiled for an hour and allowed to settle for about a further hour, after which either the bitartrate solution is decanted by means of a tap a short distance from the bottom, or the whole mass is passed through a filter-press. The liquid is left to cool in a cold place in ordinary crystallising vessels, or, better, in copper or aluminium basins, a somewhat impure and reddish-brown tartar crystallising out. Rather purer tartar may be obtained by collecting the crystals separating while the solution is cooling to 35° or 40°, small crystals being ensured by occasional stirring; the tepid mother-liquors are then decanted and crystallised in a cold place.

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[1] In many places the vinasse is placed in vats fitted with false bottoms, steam being passed in below while a spray of mother-liquor (*red liquors*) falls from above; as many hectolitres of these liquors are employed as there are quintals of vinasse. In this manner, the first solution of the tartar is obtained almost boiling and almost saturated; it is purified by percolating slowly through the vinasse (the steam expels the air and condenses). A second extraction gives a less completely saturated solution, which is utilised for further extractions. Finally, the vinasse is not pressed but is washed with water and a little hydrochloric acid to extract the calcium tartrate, exhaustion being then obtained by means of cold water (*Tarulli's method*). The mother-liquors from the crystallisation, when they become too impure or, in some cases, even after the first crystallisation, are treated with milk of lime to precipitate all the dissolved tartar, while the liquors from the second and third extractions are used for fresh quantities of vinasse.

To obtain purer solutions from the vinasse, to avoid losses occasioned by the presence of lime in the water, and to extract calcium tartrate at the same time, Ciapetti exhausts the vinasse with dilute solutions of sulphurous and hydrosulphurous acid—which do not dissolve the colouring-matters or the pectic or albuminoid substances—and allows refined, white cream of tartar (!) to crystallise out; the mother-liquors are utilised further. This method was tried in various works, but did not give the results expected of it. Extraction on the Ciapetti system may also be carried out in the series of stills used for the distillation of the vinasse (*see later*, Tartaric Acid, Gladysz Process).

The fresh vinasse or the deposits, if not to be worked up at once, may be kept for some months if tartaric fermentation—which would destroy part of the cream of tartar—is prevented, either by addition of 0·05 per cent. of sodium thiosulphate or by maintaining the vinasse strongly compressed, under chalk and sand, in wooden vats (tartaric fermentation is caused principally by *Bacillus saprogenes vini*). The yields of tartar and alcohol are determined on a small quantity (5 kilos) of the vinasse in a small Savalle distilling and macerating apparatus.

The brown mother-liquors are used repeatedly to dissolve fresh quantities of the crude tartar substances in the hot. The brown crystals are detached from the crystallising vessels by means of suitable spatulas and redissolved, in a wooden vessel similar to that previously used (with a perforated bottom for the crystals), in ten to twelve times their weight of water, which is boiled by indirect steam supplied through copper or aluminium coils. Decolorisation is effected by adding, after half an hour's boiling, about 1 per cent. of animal charcoal (well washed with hydrochloric acid and thoroughly rinsed; for very impure tartar from lees as much as 6 to 8 per cent. of animal charcoal is used). After mixing and an hour's boiling, about 1 per cent. of kaolin free from chalk (washed with HCl) is well mixed in in the hot and the liquid either filter-pressed or left for two to three hours so that the kaolin may carry down all the suspended charcoal. In some cases the solutions are clarified by adding tannin and gelatine (50 grams of the latter and 250 of tannin dissolved separately) after the kaolin and before filtration. The pale yellow, clear solution is decanted (the first and last portions, which are rather turbid, being kept separate) and crystallised in wooden crystallising vessels or in copper or aluminium basins; in three or four days the crystallisation is complete. The mother-liquors are used to dissolve fresh brown crystals, since they contain a little free tartaric acid which dissolves many of the impurities better than water does, and so results in the separation of purer crystals. After the removal of the mother-liquor, the crystals are washed repeatedly with very pure water (condensed), a trace of hydrochloric acid being added to the first washing water if the crystals show any superficial turbidity. They are finally dried on cloths in a desiccator at 60° with the help of a current of air.

In France and also in certain Italian factories, Carles has applied a method of extracting the tartar which consists in treating 100 parts of the crude, powdered tartar with 400 parts of water at 70°, containing sufficient sodium carbonate to transform all the potassium bitartrate into the highly soluble sodium potassium tartrate (1 : 1·2). This solution is decanted or filtered and treated with more than the amount of hydrochloric or sulphuric acid necessary to neutralise the soda added; this leads again to the formation of the slightly soluble potassium bitartrate, which crystallises out (96 per cent. purity) on cooling. Vinasse is also extracted more readily by this alkaline method.

The recent process of Cantoni, Chautems and Degrange (1910) refines the tartar almost in the cold and effects a marked economy of chemical products. This method serves well also for poor products (20 per cent. lees), which are heated as described above and washed first with cold sodium carbonate solution in a series of vessels, next slightly with water, and finally, slowly and systematically with dilute hydrochloric acid.

In the first case, sufficient soda is added to convert the tartar almost completely into sodium potassium tartrate, which is highly soluble and may be extracted with the minimum quantity of water. The treatment with hydrochloric acid dissolves the remainder of the tartar and also the calcium tartrate. The amount of the acid used is chosen so that, when the alkaline and acid solutions are united, it neutralises the soda first used. The hydrochloric acid solution is mixed previously with the amount of oxalic acid required to precipitate the whole of the lime present in the crude tartar as calcium tartrate, while sufficient potassium chloride is added to the alkali solution to transform all the tartaric acid, existing as calcium tartrate, into potassium bitartrate. Mixing of the two solutions in the cold results in the precipitation of almost all the cream of tartar in a white, highly pure state, and of the calcium oxalate. After filtering, the dark mother-liquors are kept for subsequent operations, while the solid residue is treated with the calculated (on the solubility of the tartar) quantity of water at 90°, a little oxalic acid being added to render the calcium oxalate less soluble. The mass is then filtered or centrifuged (if necessary, decolorised with a small amount of animal charcoal), the clear liquid, on cooling, depositing refined tartar of a purity of 99 to 99·5 per cent. The mother-liquor is used to initiate the solution of further quantities of crude tartar, etc. Oxalic acid may be recovered from the calcium oxalate.

A process which allows of the conversion of calcium tartrate into potassium bitartrate consists in boiling, say, 100 kilos of the calcium tartrate (85 per cent.) with 1500 litres of water and 53·5 kilos of potassium bisulphate (or a mixture of 35 kilos of the neutral sulphate and 24·6 kilos of sulphuric acid at 60° Bé.) for half an hour, decanting and filtering the liquid, from which pure potassium bitartrate (up to 98 per cent.) crystallises on cooling.

This process is a modification of that of Martignier (Fr. Pat. Nov. 23, 1889), who transforms calcium tartrate into normal potassium tartrate by decomposition with normal potassium sulphate; after filtration and concentration and addition of the calculated amount of sulphuric acid, the solution deposits potassium tartrate.

If the cream of tartar crystals are not pure but contain small proportions of calcium tartrate, they do not give perfectly clear solutions in water. When the pale mother-liquors from the final refining are somewhat impure, they are used in place of the brown liquor to dissolve the crude material, the highly impure brown liquors being used in the manufacture of tartaric acid or added in small amounts to the prime tartaric materials.

STATISTICS AND USES. Italy exported and imported the following quantities of tartar materials:

Year	Crude tartar and cask deposits				Wine lees				Pure cream of tartar			
	Imported		Exported		Imported		Exported		Imported		Exported	
	Tons	Value (£)	Tons	Value (£)	Tons	Value (£)	Tons	Value (£)	Tons	Value (£)	Tons	Value (£)
1906	492	17,701	16,828	605,824	Included in crude tartar, etc.				35	2,082	19	1,241
1908	106	3,587	10,405	353,773	231	2,581	8,311	93,081	66	3,564	16	948
1910	275	9,004	10,278	337,120	161	1,673	7,574	78,760	63	3,392	32	1,944
1912	172	—	8,594	—	156	—	6,169	88,834	119	8,839	—	—
1913	273	11,361	8,505	353,791	456	6,571	4,054	58,376	34	2,491	—	—
1914	360	18,694	9,964	518,107	443	6,766	5,298	80,533	332	31,901	600	57,600
1915	1,412	107,312	7,897	600,164	564	11,737	2,391	49,722	105	17,347	1,456	241,613
1916	541	41,108	4,670	354,928	2,076	43,177	40	836	18	2,921	976	161,933
1917	228	25,047	6,693	776,400	326	13,048	441	17,632	1	286	729	189,592
1918	15	1,617	6,809	789,867	384	15,344	1,041	41,656	—	—	605	157,214

The exports from Italy are sent mostly to France, Great Britain, and the United States.

The total Italian production of tartar, etc., in 1905 has been estimated at £1,600,000, the *world's production* being valued at about £2,800,000 (probably too low). Crude tartar and lees pay an export duty from Italy of 1*s.* 9*d.* per quintal, no import duty being levied; refined tartar pays an import duty of 3*s.* 2*d.* Italy contains about 200 crude cream of tartar works, but only very few manufacturing refined tartar.

Great Britain imported (usually one-half from France and one-fourth from Germany) 3200 tons of cream of tartar in 1918, 4000 in 1910, 3890 in 1912, and 3980 in 1913.

For Germany the importation (of crude tartar and calcium tartrate) and exportation (of pure cream of tartar) are (tons):

	1908	1909	1910	1912	1913
Importation . .	2691	2026	3067	4258	6310
Exportation . .	1225	1154	1783	2199	3353

In 1910 France produced 12,000 tons of crude tartar and more than 6000 tons of refined cream of tartar. The imports and exports are as follows (tons):

		1913	1914	1915	1916
Wine residues	imports . .	10,876	8,561	8,038	5,575
	exports . .	1,992	1,867	932	666
Crude tartar	imports . .	1,417	1,140	1,279	887
	exports . .	9,415	5,500	4,973	4,216
Tartar crystals, etc.	imports . .	163	26	247	26
	exports . .	—	—	—	—
Refined cream of tartar	imports . .	16	25	48	49
	exports . .	4,408	3,499	3,208	2,268

At least one-half of the refined cream of tartar is exported to Great Britain.

The United States imported 14,000 tons of cream of tartar in 1910, 13,800 in 1911, 13,000 in 1912, and 14,000 (£560,000) in 1913.

Before 1913 the United States levied an *ad valorem* import duty of 5 per cent. for low-grade and 25 per cent. for high-grade cream of tartar. After 1913 a new tariff was to come into force, but now that the war is over the question remains unsettled—as in other countries also.

The *price* of crude and refined tartar products varies widely, even in one and the same year, according to the requirements of the markets and also to speculation in raw materials and refined products.

Before the war crude cream of tartar was sold at 11½*d.* to 14½*d.* or even less per unit or kilo of the pure tartar in 100 kilos of crude product, and the refined at 1*s.* 9*d.* to 1*s.* 11*d.*

During and since the war the price of the crude material has become quadrupled and that of the refined product quintupled.

Cream of tartar is largely used in dyeing, in the bichromate mordanting of fast wool dyes, etc., and in the printing of textiles. Considerable quantities are used in the United States, Australia, Japan, China and India for preparing powder which is added to dough to render the bread light and elastic; this powder contains 69 per cent. of tartar and 31 per cent. of sodium bicarbonate.[1]

MANUFACTURE OF TARTARIC ACID. This acid is prepared by decomposing its salts (cream of tartar, lees, calcium tartrate, etc.), the dark mother-liquors and the deposits and sludges of cream of tartar factories being most commonly employed.

Attempts were at one time made to liberate the acid from its soluble salts by treating these, in hot solutions, with hydrofluosilicic acid, which separates as insoluble potassium fluosilicate, the solution of tartaric acid remaining being filtered, concentrated and crystallised. The potassium fluosilicate is treated with calcium carbonate to convert it into soluble potassium carbonate and insoluble calcium fluosilicate, which yields hydrofluosilicic acid under the action of an energetic acid. Tartaric acid has also been prepared by treating solutions of its salts with potassium carbonate and then with barium chloride, the latter precipitating the neutral potassium tartrate partly formed by the former reagent.

At the present time, however, the method most commonly used consists in treating boiling cream of tartar solutions with milk of lime or powdered calcium carbonate. In this way one-half of the tartar is converted into insoluble calcium tartrate and the other half into the soluble normal potassium tartrate, the latter being then separated as the insoluble calcium salt by addition of calcium sulphate or chloride:

$$2C_4H_5O_6K + CaCO_3 = H_2O + CO_2 + C_4H_4O_6Ca + C_4H_4O_6K_2;$$
$$C_4H_4O_6K_2 + CaSO_4 = K_2SO_4 + C_4H_4O_6Ca.$$

The acid is liberated from calcium tartrate by means of sulphuric acid:

$$C_4H_4O_6Ca + H_2SO_4 = CaSO_4 + C_4H_6O_6.$$

According to the nature of the materials employed, various procedures are adopted.

Crude tartar is freed from coarser impurities by passing through a wide-meshed sieve, heated if necessary (*see above*), ground to a fine granular condition and placed in a wooden vessel, where it is treated with eight to ten times its weight of boiling water. The mass is well mixed with a stirrer and heated to boiling by a steam jet, most of the tartar then dissolving. A paste of calcium hydroxide (sieved) is then added until a small portion of the liquid gives only slight effervescence with calcium carbonate (as a rule, 160 grams of quicklime, made into a 10 per cent. paste, are required for each kilo of potassium tartrate), the mixture being then boiled for fifteen minutes.

In this way calcium tartrate is precipitated, while normal potassium tartrate remains in solution. The latter is then precipitated as calcium salt by boiling with a slight excess of gypsum or of calcium chloride solution (300 grams of the chloride per kilo of tartrate used) for about two hours; a little precipitated calcium carbonate is finally added to precipitate the neutral tartrate as completely as possible. In some cases, however, the liquid is left slightly acid to prevent separation of iron and aluminium salts. It is, indeed, necessary to ensure the absence from the various reagents (lime, chalk, gypsum, etc.) of iron, aluminium, and especially magnesium, the latter forming magnesium tartrate, which is ultimately found as magnesium sulphate in the tartaric acid after the calcium tartrate

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[1] **Cream of Tartar in Bread-making.** When bread is made with yeast, an appreciable amount of sugar, derived from the flour, is lost owing to its conversion into alcohol and carbon dioxide. The yeast may be replaced by 500 grams of cream of tartar and 225 grams of sodium bicarbonate per 50 kilos of flour, the doughed mixture being left to stand until evolution of carbon dioxide commences; it is then divided into loaves and baked, good light bread being thus obtained. Production of CO_2 by means of bicarbonate and hydrochloric acid has also been proposed, addition of salt being then unnecessary. Some years ago Candia suggested the use of compressed CO_2 for this purpose, the composition of the dough thus remaining quite unchanged.

has been treated with sulphuric acid. The boiling liquid is kept mixed and is afterwards either allowed to cool to 40° and decanted or passed immediately to the filter-press; after repeated washings with hot and cold water, the crude, dry tartrate is placed on the market and the filtrate either rejected or evaporated to obtain the potassium chloride present. Where, however, the calcium tartrate is converted into tartaric acid, it is not necessary to filter and dry it, the tartrate, after the first decantation, being mixed with various separate amounts of water, which are drawn off when the precipitate settles. The calcium tartrate remaining may then be treated in the same vessel with sulphuric acid as described above.

The procedure is rather more complicated in the case of *wine lees* (sediments, sludge, etc.), as the tartrate cannot be extracted merely by treatment with water and filtration, owing to the presence of considerable amounts of mucilaginous protein substances (ferments), which impede filtration, so that they are either treated with concentrated sulphuric acid (60° Bé.) or heated (*see above*). The moist lees (drained in bags and pressed) contain as much as 8 per cent. of cream of tartar, or, if dried in the sun, still more.

These lees are nowadays worked by the Dietrich and Schnitzer process (1865): they are first powdered and mixed by means of stirrers and then heated for five to six hours in iron autoclaves (4 metres high and 1·4 wide for 15 quintals of lees) at 4 to 5 atmos. pressure, direct steam being admitted by copper coils and the air first allowed to escape. The albuminoids are thus coagulated, together with large quantities of colouring-matters, and the mass may then be easily filtered, but before this, it is discharged into a lead-lined wooden vessel (holding 10 to 12 cu. metres) containing 3 cu. metres of water and the amount of hydrochloric acid (20° to 22° Bé.) corresponding with the quantity of tartar previously determined (100 kilos of potassium bitartrate require 60 kilos of hydrochloric acid at 20° Bé., or 54·5 kilos at 22° Bé.). The mass is well mixed and passed through the filter-press, in which it is washed with water. The tartaric acid is then separated from the solution as calcium tartrate, as described above.

Lees may be treated economically and well by the process of Cantoni, Chautems, and Degrange described above.

To utilise the potash salts of the filtrate from the calcium tartrate, A. Alberti (U.S. Pat. 957,295, 1910) decomposes the organic substances in the hot with calcium chloride, filters and concentrates in a vacuum.

The second phase of the manufacture of tartaric acid consists in the decomposition of the calcium tartrate by means of sulphuric acid (*see above*) and in the subsequent crystallisation of the tartaric acid.

The calcium salt in the decantation or washing vessels, or as cakes from the filter-presses, is broken up and suspended in five to six times its weight of water in lead-lined wooden vessels furnished with stirrers covered with lead and with coils for indirect steam-heating. After the liquid paste has been well stirred, the sulphuric acid, previously diluted, is added in such amount that, after an hour's stirring at 60° to 70°, there is still a slight excess of sulphuric acid, detectable by the faint green coloration imparted to a solution of methyl violet. Too great an excess of sulphuric acid produces blackening of the tartaric acid solution during concentration, whilst deficiency of sulphuric acid results in the formation of turbid, impure tartaric acid crystals; when a little free sulphuric acid is present, fine shining crystals are obtained. Usually 1 kilo of sulphuric acid at 66° Bé. is employed per 3 kilos of dry calcium tartrate. The solution is boiled for a couple of hours, left to cool, and the calcium sulphate which forms separated by means of a filter-press, washed with a little tepid water (this being added to the filtrate), and then with much cold water (this being used for treating subsequent quantities of calcium tartrate). The tartaric acid solutions were at one time concentrated in shallow, lead-lined, wooden vessels containing leaden steam-coils, but nowadays concentration is carried out in vacuum pans which are similar to those described later in dealing with the sugar industry and are of hard lead and of considerable thickness.

The liquid is evaporated until it becomes almost syrupy, and is then discharged into wooden vessels containing stirrers, which cool the concentrated solution rapidly and thus cause the tartaric acid to separate in small crystals. The cold mass is quickly separated from the mother-liquor in a centrifuge, the crystals being washed with a fine spray of cold water. The mother-liquors are then concentrated until they give crystals, this process being carried out three times; they are finally treated with milk of lime to separate the residual tartaric acid as calcium tartrate, which is filtered and worked up with the other calcium tartrate. The tartaric acid crystals are dissolved in one-half their weight of boiling water (if necessary, the solution is decolorised with animal charcoal and filtered) and the liquid left to crystallise, the crystals thus obtained being centrifuged and dried on sheets of lead in a current of air at 30°; the mother-liquors are used to dissolve fresh quantities of the small crystals.

The final *yield* is about 90 to 95 per cent. of the total tartaric acid in the prime materials when these are poor (*e. g.*, lees with 20 to 25 per cent. of tartar) or 97 to 99 per cent. when richer prime materials (70 to 80 per cent. of tartar) are used.

A process still little used, but worked successfully for many years in the Montredon factory near Marseilles, is that of Gladysz (Ger. Pat. 37,352, October 15, 1885), which is based on the following observations: (1) When calcium tartrate is suspended in water and saturated with sulphur dioxide, soluble calcium bisulphite is formed and the tartaric acid liberated; (2) when this solution is heated to 66°, the sulphurous acid is expelled and all the tartaric acid precipitated as pure crystallised calcium tartrate; (3) if in (1) potassium bitartrate is used instead of calcium tartrate, potassium bisulphite and tartaric acid are formed, and on heating the liquid to 80°, sulphur dioxide is evolved and pure potassium bitartrate separated in a crystalline state; (4) potassium tartrate, when treated with calcium bisulphite, gives potassium bisulphite and calcium bitartrate; the latter separates at 100°, when the potassium bisulphite gives, with lime, calcium bisulphite and caustic potash, which can also be utilised.

In practice Gladysz proposed to suspend the tartar in lumps in lead-lined wooden vessels, and into these—hermetically sealed and arranged in a series of five or six—to pass sulphur dioxide. The solutions (10° to 12° Bé.) thus obtained are sent to the concentration apparatus, which communicates with towers to condense the sulphur dioxide (*see* Vol. I., p. 280). When the latter is completely evolved, the liquid is kept at 125° for a short time to separate crystalline calcium tartrate, which is collected by means of a centrifuge, while the solution is concentrated further and allowed to cool in shallow lead-lined wooden vessels to deposit the potassium tartrate. As a rule, however, the hot potassium tartrate solution is treated directly with calcium chloride and a little lime, so that it yields insoluble calcium tartrate, which is more easily separated. From this calcium tartrate, pure tartaric acid is then obtained in the ordinary way. Although theoretically no sulphur dioxide should be lost in this process, in practice about 15 per cent. is lost in winter and 20 per cent. in summer.

The Gladysz process, somewhat modified by Ciapetti, is used in Italy in the manufacture of tartar from vinasse, lees, etc. (*see* p. 404).

USES AND STATISTICS OF TARTARIC ACID. This acid is used in considerable quantities to replace the more expensive citric acid in the preparation of beverages, liquors, and aerated waters, and in wine-making. Large quantities are consumed in the mordanting of wool and silk, to reduce chromium salts, etc., in the printing of textiles, manufacture of dyes, photography, medicine, etc. Refined tartaric acid pays an import duty in Italy of 8*s.* per quintal and in the United States and Spain of 25 per cent. *ad valorem.*

Italy possesses the following large tartaric acid factories: at Carpi, Agnano (Pisa), Barletta, Milan, and Casalmonferrato (the last of these was transferred to Milan in 1920). The last three are the more important, and are able to produce together as much as 5000 tons per annum.

The *world's production* in 1905 was about 11,000 tons, of which Italy produced 670 tons; England and the United States, each more than 2500; Germany, about 1500; France, about 800 (1300 in 1910); and Austria-Hungary about 1000 tons. Germany exported 1700 tons of the refined acid in 1908, 2100 in 1910, 1850 in 1911, 2673 in 1912, and 2956 in 1913; the imports were 458 tons in 1910, 379 in 1911, 428 in 1912, and 325 in 1913.

For Italy the imports and exports are as follows:

		1908	1910	1912	1913	1914	1915	1916	1917	1918
Imports	tons .	138	298	146	40	20	87	26	0·7	2·5
	value, £	—	27,380	—	4,594	2,314	20,952	6,264	280	1,000
Exports	tons .	1,928	2,177	2,516	2,846	2,963	3,634	3,292	2,413	1,971
	value, £	—	196,000	—	324,467	355,536	872,256	790,132	965,080	788,400

Great Britain imported 1700 tons of tartaric acid in 1908, 2050 in 1910, 2000 in 1912, and 2300 in 1913, and exported 335 tons in 1911 and 835 in 1913.

For France the importation and exportation are as follows (tons):

	1913	1914	1915	1916
Importation	501	374	273	305
Exportation	1350	1073	1027	914

In 1907, four Russian factories, worked by a syndicate, produced 600 tons of tartaric acid and sold it at £200 per ton.

The Argentine imported 95 tons of tartaric acid in 1904, 465 in 1909, 729 in 1910, and 868 (almost three-fourths from Italy) in 1911. In 1911 a factory capable of making 330 tons per annum was erected at Buenos Aires.

The price of tartaric acid is variable for the reasons mentioned on p. 407. Some years before the war the price was about £140 per ton, in 1911 it approached £100, and during the war it rose in Italy to £360 or even £560 per ton, while after the war ended in 1919 it varied from £440 to £520 per ton.

ARTIFICIAL TARTARIC ACID. In 1889 a process was patented by Basset, and in 1891 a similar but improved one by Naquet for obtaining tartaric acid from starch (1 to 5 of water) by saccharifying with an equal weight of hot sulphuric acid (51° Bé.), then adding double this quantity of sulphuric acid and almost as much sodium nitrate and heating at 100°. When the reaction becomes very vigorous, the temperature is moderated and the heating continued at 80° to 90° for two to three days, the evaporated water being first replaced and the liquid concentrated to a syrup when evolution of gas ceases. In this manner all the saccharic acid is decomposed; the sulphuric and oxalic acids are then neutralised with calcium carbonate and the tartaric acid subsequently worked up in the usual manner by way of its calcium salt.

One hundred kilos of starch should give theoretically 140 of calcium tartrate, corresponding with 56 kilos of tartaric acid, but in practice the yield of the acid does not exceed 55 to 60 per cent. of this theoretical amount.

TRIHYDROXYGLUTARIC ACID, $CO_2H \cdot [CH(OH)]_3 \cdot CO_2H$, should exist in four stereoisomeric forms, of which the dextro-, lævo- and racemic (m.-pt. 127°) compounds are known. They are obtained by the oxidation of xylose or arabinose, and, on reduction, give glutaric acid, their constitution being thus confirmed.

SACCHARIC ACID, $CO_2H \cdot [CH(OH)]_4 \cdot CO_2H$, forms ten stereoisomerides, which are all known and are closely related to the sugars. Saccharic acid is formed as a rule in the oxidation of sucrose, glucose, mannitol, and starch (*e. g.*, with nitric acid). It is deliquescent and soluble in water, and when heated or fused is converted into *saccharone*, which is a dextro-rotatory lactone melting at about 150°.

MUCIC ACID, $CO_2H \cdot [CH(OH)]_4 \cdot CO_2H$, is the stereoisomeride of saccharic acid which is constantly inactive. It is obtained on oxidising lactose, dulcitol, gum, etc., and forms a white powder very slightly soluble in water.

KETONIC DIBASIC ACIDS

Esters of these acids, like those of β-ketonic acids (ethyl acetoacetate, etc.; *see* p. 396), show both ketonic and acid decompositions, and also a new one in which carbon monoxide separates.

MESOXALIC ACID (Dihydroxymalonic Acid), $CO_2H \cdot CO \cdot CO_2H + H_2O$ or $CO_2H \cdot C(OH)_2 \cdot CO_2H$, shows ketonic behaviour in agreement with the first formula, but the molecule of water cannot be separated from the deliquescent prisms even at 100°, and, further, derivatives (esters, etc.), are known which correspond better with the second formula, whilst the latter also explains well why mesoxalic acid, when heated with water, loses CO_2 and gives glyoxylic acid, $CO_2H \cdot CH(OH)_2$. The structure of the acid likewise follows from its formation by the action of barium hydroxide on ethyl dibromomalonate:

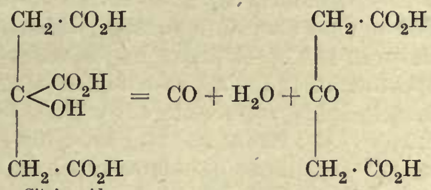
$$CBr_2(CO_2C_2H_5)_2 + Ba(OH)_2 = BaBr_2 + C(OH)_2(CO_2C_2H_5)_2.$$

Its ketonic constitution is confirmed also by the fact that it gives tartronic acid, $CO_2H \cdot CH(OH) \cdot CO_2H$, on reduction.

OXALACETIC ACID (Butanonedioic Acid), $CO_2H \cdot CH_2 \cdot CO_2 \cdot CO_2H$, is not known in the free state, but is formed as ester by condensation of ethyl oxalate and ethyl acetate in presence of sodium ethoxide (*see* Ethyl Acetoacetate). It also splits up in two ways according as it is treated with dilute sulphuric acid (giving pyruvic acid, CO_2, and alcohol) or with alkali (giving oxalic and acetic acids). Being a ketone, it forms an oxime.

The alcoholic solution is coloured dark red by ferric chloride and hence corresponds with the enolic form, $C_2H_5 \cdot O \cdot CO \cdot CH : C(OH) \cdot CO_2C_2H_5$. This ester, like ethyl acetoacetate, is used in many syntheses, the hydrogen of the methylene group being replaceable by sodium, etc.

ACETONEDICARBOXYLIC ACID (Pentanonedioic Acid), $CO_2H \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2H$, forms crystals which melt at 135°, losing $2CO_2$ and giving acetone. It is formed by the action of concentrated sulphuric acid, in the hot, on citric acid :



$$\begin{array}{c}CH_2 \cdot CO_2H\\ |\\ C<^{CO_2H}_{OH}\\ |\\ CH_2 \cdot CO_2H\end{array} = CO + H_2O + \begin{array}{c}CH_2 \cdot CO_2H\\ |\\ CO\\ |\\ CH_2 \cdot CO_2H\end{array}$$

Citric acid

The constitution of citric acid is shown by its formation from acetonedicarboxylic acid by the action of hydrogen cyanide and subsequent hydrolysis.

The hydrogens of the two methylene groups are replaceable by sodium, so that this acid may be used in syntheses similar to those effected by ethyl acetoacetate.

DIHYDROXYTARTARIC ACID, $CO_2H \cdot CO \cdot CO \cdot CO_2H + 2H_2O$, or, better, $CO_2H \cdot C(OH)_2 \cdot C(OH)_2 \cdot CO_2H$, melts and decomposes at 98° and forms a sodium salt, which is sparingly soluble and decomposes readily into CO_2 and sodium tartronate, $CO_2H \cdot CH(OH) \cdot CO_2Na$.

It is obtained by the action of nitrous acid on an ethereal solution of pyrocatechol, guaiacol, etc., and also by the spontaneous decomposition of nitrotartaric acid. Sodium bisulphite converts it into glyoxal, while with hydroxylamine it forms the dioxime corresponding with the diketonic form. With phenylhydrazinesulphonic acid, it forms *tartrazine*, a beautiful yellow colouring-matter largely used in dyeing wool and silk.

Of the higher ketonic acids the following may be mentioned: *hydrochelidonic acid* (*acetonediacetic acid*), $CO(CH_2 \cdot CH_2 \cdot CO_2H)_2$; *diacetosuccinic acid*, $\begin{array}{c}CH_3 \cdot CO \cdot CH \cdot CO_2H\\ |\\ CH_3 \cdot CO \cdot CH \cdot CO_2H\end{array}$; and *diacetylglutaric acid*, $CH_2<^{CH(CO \cdot CH_3) \cdot CO_2H}_{CH(CO \cdot CH_3) \cdot CO_2H}$ the esters of which give rise to tetrahydrobenzene derivatives or, in presence of ammonia, to pyridine derivatives.

G. POLYVALENT TRIBASIC HYDROXY-ACIDS

ETHANETRICARBOXYLIC ACID, $CO_2H \cdot CH_2 \cdot CH(CO_2H)_2$, and **ASYM. PROPANETRICARBOXYLIC ACID**, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H)_2$. These two acids are stable in the form of esters, but in the free state they readily decompose, liberating CO_2 and forming dibasic acids.

TRICARBALLYLIC ACID (Symm. Propanetricarboxylic or Pentadioic-3-methyloic Acid), $CO_2H \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, melts at 163° and is very soluble in water.

It is found in unripe beets and occurs abundantly in the deposits of the vacuum pans of sugar factories. Synthetically it is obtained from *aconitic acid* [1] by the addition of hydrogen and from citric acid, which loses its hydroxyl group when treated with hydriodic acid.

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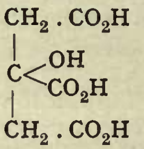
[1] **Aconitic Acid** is the corresponding unsaturated acid, $\begin{array}{l}CH \cdot CO_2H\\ \|\\ C \cdot CO_2H\\ |\\ CH_2 \cdot CO_2H\end{array}$. It melts at 191°, and is readily soluble in water; it is an energetic acid and is converted into tricarballylic acid by nascent hydrogen. It is prepared by heating dry citric acid, which loses a molecule of water.

It occurs naturally in the sugar-cane, beet, *Aconitum napellus*, etc.

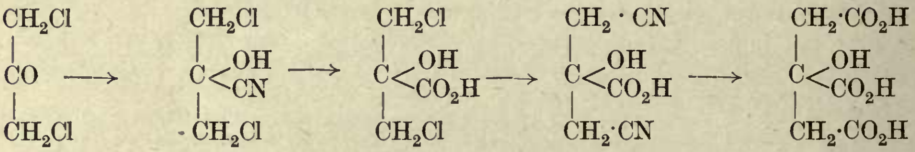
Its constitution is shown by its synthesis from glycerol by way of the tribromhydrin and tricyanohydrin, $C_3H_5(CN)_3$, the latter being hydrolysed

CITRIC ACID,


$$\begin{array}{l} \mathrm{CH_2 . CO_2H} \\ | \\ \mathrm{C}<\begin{smallmatrix}\mathrm{OH} \\ \mathrm{CO_2H}\end{smallmatrix} \\ | \\ \mathrm{CH_2 . CO_2H} \end{array}$$

This acid is deposited from its aqueous solutions—if these are not too hot—in large, rhombic prisms containing $1H_2O$, which is given up partly in dry air and completely at 135°. It melts in its water of crystallisation at 135° and, when anhydrous at 153° and at a higher temperature decomposes into aconitic and itaconic acids, citraconic anhydride, CO_2, and acetone. It is readily soluble in water (135 : 100 at 15° and 200 : 100 at the boiling-point) [1] or alcohol (53 : 100 at 15° and about double as much in 80 per cent. alcohol), and to a slight extent in ether (9 : 100). It was discovered by Scheele in 1784 and studied by Liebig in 1838. It occurs abundantly in nature in the lemon (4·5 per cent. in the unripe lemon), orange, gooseberry, and other fruits, and in small quantities in cows' milk, the shoots and leaves of the vine, tobacco, and fungi, and as calcium salt in the beet, willow, etc.

Industrially it is obtained by the lime method described later (*see* p. 415). Synthetically it may be prepared from acetonedicarboxylic acid by the action of hydrocyanic acid and subsequent hydrolysis. The constitution thus indicated is confirmed by its formation from symm. dichlorhydrin, $CH_2Cl \cdot CH(OH) \cdot CH_2Cl$, which on oxidation gives symm. dichloracetone, and hence by the introduction of cyanogen groups and hydrolysis yields citric acid :



$$\begin{array}{lclclclcl} \mathrm{CH_2Cl} & & \mathrm{CH_2Cl} & & \mathrm{CH_2Cl} & & \mathrm{CH_2 \cdot CN} & & \mathrm{CH_2 \cdot CO_2H} \\ | & & | & & | & & | & & | \\ \mathrm{CO} & \longrightarrow & \mathrm{C}<\begin{smallmatrix}\mathrm{OH} \\ \mathrm{CN}\end{smallmatrix} & \longrightarrow & \mathrm{C}<\begin{smallmatrix}\mathrm{OH} \\ \mathrm{CO_2H}\end{smallmatrix} & \longrightarrow & \mathrm{C}<\begin{smallmatrix}\mathrm{OH} \\ \mathrm{CO_2H}\end{smallmatrix} & \longrightarrow & \mathrm{C}<\begin{smallmatrix}\mathrm{OH} \\ \mathrm{CO_2H}\end{smallmatrix} \\ | & & | & & | & & | & & | \\ \mathrm{CH_2Cl} & & \mathrm{CH_2Cl} & & \mathrm{CH_2Cl} & & \mathrm{CH_2 \cdot CN} & & \mathrm{CH_2 \cdot CO_2H} \end{array}$$

Citric acid was prepared some years ago (Fabrique de produits chimiques de Thann et de Mulhouse) by Wehmer's biological process (Ger. Pat. 72,957 of 1893), according to which glucose is fermented by certain moulds (*Citromyces Pfefferianus* and *Glaber*, and *Mucor pyriformis*), the yield being about 55 per cent. of the sugar.[2]

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[1] The following table gives the percentage by weight in aqueous solutions of different densities :

Degrees Baumé . .	2	4	6	10·5	12	14	18	22	26	28	30	32	34
Per cent. of citric acid .	4	8	12	20	22	26	34	42	50	54	58	62	66

[2] The formation of citric acid by the action of micro-organisms on sugar was studied in detail also by Mazè and Perrier in 1904, by Herzog and Polotzky in 1909, and by Buchner and Wüstenfeld in 1909 with *Citromyces citricus*. All these authors found that such organisms are able to live in highly acid media and that, under certain conditions, especially when there is a scarcity of nutrient nitrogenous substances, they can transform as much as 50 per cent. of the sugar into citric acid. A current of air passed through the fermenting liquid does not aid the development of the organisms, but at the same time does not oxidise the citric acid formed; lack of air, however, retards the fermentation. The presence of inorganic ammonium salts and of calcium carbonate results in a good yield and in good separation of calcium citrate. Various tests were made with 20 per cent. solutions of sugar (sucrose, which is rapidly inverted) containing 0·5–1 per cent. of inorganic salts (ammonium phosphate or nitrate, etc.); in ten to twelve days or, in some cases, in thirty-five days, 40 to 50 per cent. of the sugar undergoes conversion into calcium citrate (Wehmer, 1912). The formation of the citric acid by direct oxidation (as occurs in acetic or oxalic fermentation) is excluded, and Mazè advances the hypothesis that the acid is derived rather from the decomposition of the protein substances forming the ferments themselves, whilst Buchner assumes the intermediate formation of parasaccharinic acid.

Wehmer (1913) confirms the observation of earlier experimenters that calcium citrate is

When heated for a long time with water, citric acid forms a little aconitic acid, into which it is transformed completely by concentrated hydrochloric acid. It is readily oxidised to acetone, oxalic acid, and carbon dioxide.

Like tartaric acid, citric acid hinders the precipitation of the metallic hydroxides from their salts by ammonia.[1]

Citric acid is used in large quantities for lemonade and in pharmacy and for effervescent drinks (citrate of magnesia); it is employed also in dyeing and in textile printing. It is used also in aqueous solution (or as fresh lemon juice) as a substitute for vinegar. It is often employed, in preference to tartaric acid, to increase the acidity of wine so as to improve its colour and keeping qualities (100 grams per hectolitre is sufficient, whereas about 400 grams of tartaric would be necessary to produce the same effect, since two-thirds of it undergoes precipitation as potassium bitartrate). A certain amount of citric acid is used in the analysis of superphosphates.

CITRUS INDUSTRY

Citric acid is manufactured from the juice of lemons yielded especially by the following three plant species: *Citrus limonium*, *Citrus bergamia* (*bergamot*), and *Citrus limetta* (or wild lemon cultivated by the British in Guiana and the West Indies). Lemons are cultivated most extensively in Sicily and Calabria, and to a considerable extent also in Spain. The cultivation is of little importance in Greece, the Sandwich Islands, and the West Indies, but is rapidly increasing in Australia. During recent years the production of oranges and lemons has made rapid strides in California and in Florida,[2] where it is

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obtainable in good yield also from glycerol, and finds also that citric acid is produced only as calcium citrate (*i. e.*, in presence of calcium carbonate) and never as free acid, possibly because the latter undergoes instantaneous decomposition or transformation into other substances (not into organic acids); in any case the biological formation from glycerine denotes the possibility of a synthetic process, which is somewhat rare (*see* p. 137). From lactose and ethyl alcohol citric acid has not been prepared.

According to Zahorski (U.S. Pat. 1,069,168, 1913) citric acid may be obtained from sugar (glucose, levulose, etc.) by adding 15 per cent. of citric acid to a culture of *Sterigmatocystis nigra* and using this culture for the gradual seeding of the saccharine solution.

[1] **Tests and Reactions for Citric Acid.** *Denigès' reaction* is characteristic and serves to detect small quantities of the acid; the solution is heated to boiling with one-twentieth of its volume of *Denigès' reagent* (5 grams of mercuric oxide, 80 c.c. of water, and 20 c.c. of concentrated sulphuric acid), 3 to 10 drops of approximately decinormal potassium permanganate solution being added; a white, crystalline precipitate is formed immediately even with traces of citric acid. The reaction is not masked by the presence of tartaric, oxalic, malic, sulphuric, or phosphoric acid, although the amount of permanganate used must then be slightly increased.

Häussler (1914) gives the following reaction for detecting small amounts of citric acid even in presence of other organic acids (proteins and sugars are first eliminated by successive treatment with lead acetate, H_2S and calcium carbonate): 2 c.c. of the dilute citric acid solution (even 0·1 per cent.) is evaporated to dryness in a dish with 2 c.c. of alcohol containing a little vanillin, 3 to 4 drops of 25 per cent. sulphuric acid being added to the residue and the dish heated for fifteen minutes on a water-bath: the mass then becomes an intense violet and dissolves in water to a green solution, which, even in high dilution, is coloured an intense red by addition of ammonia.

The presence of tartaric acid—which is a common adulterant—in citric acid may be detected by the addition of potassium acetate, the acid potassium citrate thus formed being readily soluble, whilst acid potassium tartrate is only slightly soluble. Minimal quantities of tartaric acid may be also detected as follows: 1 gram of the powdered substance is heated for a few minutes on the water-bath with 1 c.c. of 20 per cent. ammonium molybdate solution and a few drops of 0·25 per cent. hydrogen peroxide solution; in presence of even 0·001 gram of tartaric acid, a bluish coloration is obtained. The presence of oxalic acid is easily discovered, since *in the cold* and in ammoniacal solution calcium oxalate is insoluble, whilst calcium citrate is soluble.

[2] The lemon orchards in Sicily are found especially on the coast from Palermo to Cefalù (about one-fifth of the total production of lemons and oranges) and on the coast near Messina (more than double that of Palermo-Cefalù), usually on irrigated lands, but sometimes in cool non-irrigated districts. The stocks are obtained from the seed of the wild orange (called by the Sicilians *arancio agro*, or sour orange). The plants from these seeds are planted out in the orchards in their third year and are placed from 3 to 5 metres apart, according to the nature of the soil, to the wind, and to custom. After a year the stock is grafted from an adult plant. Fructification occurs after a further three years and reaches its maximum in ten years. The flowering

already about double that of Sicily. It is pleasing to note that plantations of oranges alone are being more and more largely replaced by those of lemons.

In German East and West Africa, plantations of lemons were advantageously replacing those of rubber before the war.

Only the refuse lemons (one-fourth of the total production) are used for the manufacture of citric acid, as they cost only one-half as much as the picked fruit.

The first operation to which the lemons are subjected is peeling, a workman removing the peel with three cuts of a knife, cutting the lemon in two and throwing it into a tub; the peel is collected separately for the preparation of essence. A skilled operative can peel more than 4000 lemons a day. From 8000 lemons, pressed in a suitable press, 700 litres of juice, containing 4·5 to 6 per cent. of citric acid, are obtained; only 9 to 10 per cent. of the total acid exists as calcium citrate.[1] The juice does not keep well (better if

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of the lemons on the same plant is progressive and lasts the whole of May; from the latter half of June to the beginning of October the plants are watered every fortnight. The maturation of the fruit is gradual from November to the end of April and the harvest is gathered in three periods, the best fruit being those of the middle one—December to February; the last fruit, plucked in April and the beginning of May, are poorer in juice and thicker in the peel. In the coast district of Messina, the harvest finishes at the beginning of March.

Lemons have also been forced in Sicily during the past few years, the highly valued summer fruit being thus obtained; these are called *verdelli* (high quality) and *bianchetti* (lower quality). In this case the plants are not watered during June and July, the leaves withering and all the young fruit falling. In August, water in abundance is given at intervals, and sodium nitrate applied as fertiliser. The plant then suddenly becomes very vigorous, and in a few days is covered with new flowers, the fruit ripening rapidly from the end of May to the close of the summer, and that gathered in June or July being of the highest quality. Such plants give an increased crop, especially if manured, and the fruit commands more than double the ordinary prices. This procedure is followed in orchards where the soil is not moist and can be left to dry completely and where the lemons are not alternated with oranges or other crops requiring watering.

Under favourable conditions, a good lemon plant should yield on an average 1000 lemons a year (some very large plants give several thousands). The price varies considerably, 8*s.* to 16*s.* per 1000 being paid for the fruit on the tree and as much as 24*s.* for the gathered fruit; forced lemons cost at least 20*s.* per 1000, the price in 1907 exceeding 40*s.* The cost of gathering, packing, and freight to the port varies from 1*s.* 7*d.* to 3*s.* 2*d.* per 1000. The *refuse lemons*, which form about one-fourth of the crop (or more if the demand for lemons is small), cost about half as much as the other fruit (5*s.* to 6*s.* per 1000 on the average), although on rare occasions the price reaches 8*s.*, and in 1908, at the height of the crisis, it fell to 2*s.* per 1000.

[1] *Fresh lemon juice* contains also 7 to 9 per cent. of glucose, 0·2 to 0·8 per cent. of saccharose (according as the lemons are sour or ripe), certain extractive, gummy, and pectic substances (about 0·2 per cent. for ripe and 0·8 per cent. for unripe fruit), and about 0·5 to 0·7 per cent. of inorganic salts. The presence of these substances renders it impossible to crystallise the citric acid merely by concentrating the juice, even when all the glucose is transformed into alcohol (5 to 6 per cent.), so that, even at the present time, the citric acid is separated by Scheele's classical and rather costly process, according to which it is first converted into calcium citrate. The high price of fuel has prevented the establishment of the citric acid industry in Sicily, and the preparation of the acid has been monopolised for a long time by England and, at the present time, largely by Germany. Both these countries receive the raw material from Sicily, to a small extent as lemons packed in barrels containing sea-water, partly as concentrated juice (*agro cotto*), but mostly as calcium citrate.

In consequence of the development of lemon-growing in Spain, and especially in California and Australia, and also owing to an agreement entered into by the manufacturers of citric acid, the condition of the Sicilian growers became so critical that in 1903 the Italian Minister of Agriculture offered a prize of £6000 for improvements in the industry or new processes of value to the cultivators. This sum was largely wasted by Commissions who achieved nothing or by rewarding certain favoured individuals. However, at the end of 1904, Professor Restuccia, of Messina, announced to the Government the discovery of a process for the direct extraction of citric acid by simple concentration of the juice, to which was previously added a trace of a substance—the nature of which he did not reveal (picric acid !)—and a little animal charcoal, but this process only led to further waste of money.

In 1910, Peratoner and Scarlata suggested the following new process for extracting the essence and citric acid from the lemons directly, without conversion of the acid into the calcium salt. The juice obtained by squeezing the minced lemons in hydraulic presses is partly distilled in a vacuum on a water-bath at 60° to recover the essence and then concentrated *in vacuo* at 70° until it acquires a syrupy consistency (one-tenth of the original weight). When the syrup is cold, all the citric acid is extracted by treatment with a mixture of alcohol and ether, in which many of the impurities are insoluble. The alcohol and ether are recovered by distillation, and the residue diluted with a little water, filtered, and concentrated *in vacuo*; after standing for twelve to twenty-four hours it sets to a yellowish red crystalline mass which, after defecation and decolorisation in the ordinary way (animal charcoal, etc.), gives pure colourless crystals, pasteurised at 63° to 65°), and is usually concentrated at once in open pans with direct-fire heating until the specific gravity reaches 60° on the citrometer (1·2394, or 28° Bé.), and the product represents a blackish decoction containing 300 to 400 grams of citric acid per litre (that from the bergamot of Calabria and Messina contains 300 grams, while that produced in the Sandwich Islands and in the Republic of Dominica from lemons of the limetta species has a density of 1·32 and contains about 575 grams of citric acid per litre). The boiling decoction is passed through a cloth and is collected in casks for transport.

The commercial value of the juice (*agro cotto*) depends on the content of citric acid, and is determined either by diluting the juice and titrating with normal caustic soda or by precipitating in the hot as calcium citrate and weighing the latter. This estimation is preceded by a qualitative examination to ascertain if salt has been added to increase the specific gravity (test with silver nitrate in presence of a little nitric acid) or if sulphuric or hydrochloric acid has been added to raise the degree of acidity (test with silver nitrate or barium chloride in presence of a little nitric acid).

In the large modern factories, the juice is treated in almost the same manner as in the manufacture of tartaric acid (*see* p. 407): into 100-hectolitre masonry vessels provided with stirrers and cold-water coils are placed 20 hectolitres of concentrated juice and 80 hectolitres of water, the liquid being then well mixed for thirty minutes and allowed to ferment, the glucose being thus converted into alcohol and the juice clarified. By passing very cold water through the coil the temperature of the liquid is lowered to 5°, and a large part of the dissolved and suspended extractive and mucilaginous matters separated; in presence of a little tannin, these matters coagulate and do not redissolve (50 litres of sumach extract at 10° Bé. are sufficient, the liquid being stirred for fifteen to twenty minutes immediately after the addition). The solution is then passed to the filter-presses and thence into 20-hectolitre wooden vats or into brickwork vessels similar to the preceding ones, but provided with perforated coils for direct-steam heating. The boiling liquid is now neutralised exactly with dense milk of lime or with powdered calcium carbonate. The latter causes frothing and sometimes overflow of the liquid, but precipitates a purer calcium citrate, whilst the hydroxide throws down many pectic and colouring matters. In some cases two-thirds of the acidity is neutralised with calcium hydroxide and the remainder by the carbonate. For every 100 kilos of citric acid present (titrated) 45 kilos of quicklime (57 of slaked lime or 80 of the carbonate) are added. After stirring while hot, the insoluble tricalcic citrate—which forms immediately—is passed at once through the filter-presses and washed for ten minutes with very hot water, for ten minutes with tepid water, and for five minutes with cold water, which should remain almost colourless. In some parts of Sicily, *calcium citrate* is prepared in a primitive method (with slaked lime often containing magnesia, which yields soluble magnesium citrate, this being lost) and is sold dry with a content of 64 per cent. of citric acid. 300 kilos of calcium citrate of this strength require, on the average, 100,000 lemons, the peel of which yields 37 kilos of essence, selling at 6*s.* 4*d.* per kilo.[1] The total cost of manufacturing calcium citrate and essence

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the yield being 60 to 70 per cent. The remaining acid may be separated from the mother-liquor as citrate.

In spite of the favourable opinion expressed by Professors Garelli and Paternò, this process does not seem to have been applied practically.

Meanwhile the crisis in the citrus industry, which had apparently lessened as a result of the good crops and prices of 1906 and 1907, became aggravated in 1908 owing to the diminished demand for lemons, to the American crisis, to the agreement between the producers of citric acid to limit the amount of raw material required—thus lowering prices and exhausting the usual stocks of treated products—and, finally, to the abundant production, since refuse lemons did not sell for 2*s.* 6*d.* per 1000 at the beginning of 1908 and did not pay for gathering.

Various measures have been taken by the Italian Government to protect the citric acid industry in Sicily, but it should be possible, in the present advanced condition of technical chemistry, to develop this industry without such aid. The sulphuric acid required is now made in Sicily itself, and by the use of multiple-effect evaporating plant, the consumption of coal may be reduced to a minimum. In 1911 a large citric acid factory was erected in the vicinity of Palermo by the firm of Goldenberg, from Winckel, near Wiesbaden (*see later*).

[1] *Oil of lemon* is extracted from the skin and peel by pressing the latter by hand against a sponge and then separating the liquid from the sponges; this liquid deposits the residues on standing and is afterwards decanted off and filtered. In place of this hand-pressing, which yields 0·15 per cent. of oil, special machines are used in some factories. From the waters (on standing) and from the residues remaining after decantation (by pressing), an inferior oil is recovered. Distillation of such waters yields *distilled oil*, which is not of very high quality.

from 100,000 lemons was, before the war, about £10. The cakes of calcium citrate from the filter-presses are mixed in 20-hectolitre lead-lined vessels with 15 hectolitres of cold water, the lime of the citrate being then neutralised exactly with dilute sulphuric acid (1 : 5) (with 100 kilos of citric acid in the juice correspond 400 kilos of this dilute acid); a slight excess of sulphuric acid is always added, since the presence of unaltered calcium citrate would hinder the crystallisation of the citric acid.

The acid is added in portions at the rate of 5 litres per minute, the liquid being kept well mixed and direct steam applied through a perforated leaden coil. The mass is boiled for ten to fifteen minutes, the steam being then suspended and the whole mixed for thirty minutes. The calcium sulphate is then removed by means of a filter-press and is washed with 200 litres of boiling water, which is added to the first filtrate, and then with cold water, which is afterwards used for treating fresh calcium citrate. The citric acid solutions from the filter-presses contain only minimal quantities of sulphuric acid and certain blackish extractive matters. Concentration of the solution was formerly carried out in lead-lined wooden vessels, 4 metres long, 2 metres wide, and 25 cm. deep, containing closed steam coils. Evaporation should be rapid and the temperature should never exceed 65° to 70°. When the liquid reaches 46° (sp. gr. 1·3), almost all the calcium sulphate previously remaining in solution separates; the clear liquid is then siphoned into a similar vessel underneath, the concentration being continued until a crystalline skin forms at the surface of the liquid, which is next transferred to wooden crystallising vessels, 2 metres × 70 cm. × 20 cm. (deep); the inner surface is polished with plumbago. After two days, the dark brown mother-liquors are removed and the yellowish-brown crystals centrifuged. In order to separate traces of dissolved iron from the mother-liquor, this is treated with a little potassium ferrocyanide and filtered; two or three further crops of dark-coloured crystals are obtained, the very dark mother-liquor finally obtained being added to fresh lemon-juice.

In modern factories the citric acid solution, freed from calcium sulphate by filter-pressing, is concentrated in vacuum apparatus, just as in the sugar and tartaric acid industries, the density 45° to 50° Bé. in the hot being attained. In this way, the temperature does not exceed 60° to 65°, and with a triple-effect apparatus not only rapidity, but also economy of fuel is attained (*see* Vol. I., pp. 563, 568, and also section on Sugar).

In order to remove the calcium sulphate remaining in solution, the concentration is effected in two phases: in the first to 26° to 28° Bé., the liquid being then cooled in suitable vessels in which the gypsum deposits; the residual liquid is then concentrated further to 48° to 50° Bé. This liquid is discharged into the crystallising vessels, which are of lead-lined wood and of large surface; the mother-liquors are reconcentrated and recrystallised two or three times, and are finally worked up to crude calcium citrate. The blocks of crystals left in the crystallising vessels are broken up with wooden mallets and centrifuged.

In 1912, Messrs. Schimmel and Company obtained a yield of 0·3 per cent. of the oil from the peel by chopping the latter fine, making a liquid paste with water and distilling at a pressure of 50 to 60 mm.; oil thus prepared does not keep so long as the pressed oil (at most a year). Immature lemons gathered in December–February yield the finest essence (about 450 grams per 1000 lemons). The oil is stored in tinned copper vessels and is sold by the old English pound of 12 ounces or 318 grams. Its density is 0·854 to 0·861, and its rotatory power + 60° to + 64° in a 10 cm. tube at 20°, and it distils mostly between 173° and 178°. It is yellow and undergoes change in the air and light. It dissolves easily in absolute alcohol, ether, benzene, or 5 vols. of 90 per cent. of alcohol. It contains about 90 per cent. of *limonene* and 5 to 8 per cent. of *citral*, and it is often adulterated with oil of turpentine, lemon terpenes or oil of orange. By a law passed in 1897, such adulteration is forbidden.

Deterpened essence, obtained by distilling from the oil in a vacuum 80 to 90 per cent. of the terpenes and distilling the residue in a current of steam, is a yellow oil of sp. gr. 0·89, with an intense smell of lemons, and is highly soluble in alcohol; it consists mostly of citral.

Its exportation, for making perfumes, pastry and beverages is as follows (kilos):

	1908	1910	1912	1913	1914
Oil of orange .	173,265 (£152,473)	143,285	53,803	48,103	42,838
,, bergamot .	74,842 (£95,798)	64,788	71,343	63,093	61,757
,, lemon .	476,842 (£228,884)	425,076	517,596	456,303	603,000

	1915	1916	1917	1918
Oil of orange .	70,672	96,057	72,347	312,820 (£557,948)
,, bergamot .	105,553	157,165	133,800	821,809 (£2,136,703)
,, lemon .	744,000	655,522	522,486	1,629,740 (£717,086)

The brown crystals first obtained are refined and decolorised by dissolving them in rather more than double their weight of water (to a solution of 20° Bé.) and boiling the solution with animal charcoal previously treated with hydrochloric acid, as already mentioned in considering the refining of tartaric acid (p. 404).

The hot liquid is filter-pressed under low pressure and is re-filtered until it becomes clear and free from particles of charcoal. The filtrate is concentrated in a vacuum at about 60° to 65° until crystals of citric acid form, and is then heated to 90° and discharged into lead-lined wooden crystallising vessels, in which it is stirred at intervals so as to obtain small crystals; after forty-eight hours these are centrifuged and washed in the centrifuge with pure citric acid solution, just as is done with sugar (*see later*).

If chemically pure citric acid free from metals is required, the concentration is carried out in thickly-tinned vessels and the crystallisation in wooden vessels; the traces of iron present are eliminated by addition of a little potassium ferrocyanide and sodium sulphide.

In all the washing and refining operations, pure water with little hardness is always employed.

STATISTICS AND PRICES. The importance of the Italian citrus industry is shown by the following figures:

	1909	1911	1913	1914	1915	1916	1917	1918
Output of citrus fruits (tons) .	8,400	7,865	8,765	8,016	7,591	7,000	—	—
Area under cultivation (hectares)	—	113,000	108,400	—	108,400	—	—	—
Exportation of oranges (tons) .	110,899	128,343	130,600	133,080	129,161	104,290	34,662	42,558
,, value, £ . .	443,600	924,080	1,044,802	1,330,805	1,291,614	1,251,480	830,856	406,880
,, of lemons (tons) .	256,063	258,689	304,541	308,389	204,992	209,804	150,291	91,169
,, value[1] £ . .	921,826	1,448,660	1,949,062	2,220,400	1,639,938	1,678,440	2,104,072	2,176,368

Spain exported 92,900 tons of *oranges* in 1889, 300,000 tons in 1899, 470,400 tons in 1908, and 500,000 tons (about £2,200,000) in 1912.

Before the war France produced about 2000 tons of *oranges* per annum.

In 1912 California exported 400,000 tons of *oranges*.

In Florida the *orange* crop amounted to about 170,000 tons (5,000,000 boxes) in 1894–1895, but the exceptional frost of the following winter destroyed almost all the trees and the crop was reduced to 2500 tons. The trees were afterwards replaced and the crop reached about 165,000 tons (£880,000) in 1909 and almost 270,000 tons in 1912–1913.

The *citric acid* imported into and exported from Italy (Calabria and Sicily) was as follows:

	1908	1910	1912	1913	1914	1915	1916	1917	1918
Imports (tons)	164	109	127	105	32	18	26	—	—
Value, £ .	24,332	—	18,870	—	7,040	5,370	7,890	—	—
Exports (tons)	2·3	0·8	2·3	220	599	755	1,045	832	754
Value, £ .	—	—	—	32,634	131,736	226,650	313,380	349,440	316,596

The output of *citric acid* in Italy in 1912 was still below 200 tons, and in 1914 it reached 800 tons, the capacity of the factories being 1600 tons.

The Sicilian exports and imports of *calcium citrate* (in casks called *pipes*, holding 305 kilos)[2] were as follows (especially to the United States, France, and Great Britain):

	1905	1908	1910	1912	1913	1914	1915	1916	1917	1918
Tons . .	4126	7710	6476	7680	3813	5688	6704	7279	5838	3736
Value × £1000	181	401	414	488	242	428	509	553	724	463

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[1] While in other years the picked lemons for use as fruit sold for 12*s.* or even 16*s.* per 1000 (*i. e.*, 1½ *cantaros* = about 125 kilos), and the forced fruit for as much as 32*s.*, the quotations in July 1908 were as follow: ripe lemons (gathered in winter and spring), 5*s.* 4*d.* to 8*s.* per 1000; verdelli, 17*s.* 6*d.* to 20*s.*; bianchetti, 8*s.* to 10*s.*; for pressing, 2*s.* to 2*s.* 4*d.* Subsequently prices have always been higher.

[2] M. Spica (1910) has suggested a simple, rapid, and exact method for the *analysis of calcium citrate*, the content of citric acid being obtained from the volume of carbon monoxide generated when the citrate is heated with concentrated sulphuric acid. Two grams of the citrate, moistened in a flask on the water-bath, are treated with 25 c.c. of concentrated sulphuric acid. By means of a current of carbon dioxide, all the carbon monoxide is driven into a nitrometer similar to that illustrated in Fig. 16 (p. 11), the carbon dioxide being absorbed in caustic soda. Each cubic centimetre of CO at 0° and 760 mm. corresponds with 0·009407 gram of citric acid, $C_6H_8O_7 + H_2O$; the method cannot be used with citrate adulterated with oxalate or tartrate.

The output of *calcium citrate* in Sicily in 1913 was 6000 tons, besides 800 pipes of concentrated juice; in 1914 the output was 6687 tons, and in 1918, 9087 tons (*see note*, p. 414). The mean price fixed was £52 per ton in 1905, £80 in 1907, £50 in 1909, and £53 12*s.* in 1910. In 1909, owing to the economic crisis, exportation diminished considerably and in certain months the price fell to £40 per ton. During the war the sale price for the citrate (64 per cent.) was fixed at £280 per ton for the years 1917–1919.

The *agro cotto* exported in 1905 amounted to 1200 tons (£35,520), and in 1908 to 750 tons (£22,000); subsequently practically only calcium citrate was exported.

In 1913, the freight for calcium citrate from Sicily to Marseilles was about 10*s.* per ton, and to London 16*s.*

In 1903, 281 works in Calabria and Sicily for the preparation of *agro cotto* employed a total of 4000 workmen and 240 h.p.

The annual production of refined citric acid in Europe was about 4000 tons in 1913, and the price varied from £108 to £140 per ton. In general the price rises and falls with that of tartaric acid, the difference between the prices of the two acids being due to the different degrees of acidity (3 carboxyls in one case and 2 in the other) and molecular weights [152 for tartaric acid and 210 for citric acid (+ H_2O)].

If all the juice transformed into calcium citrate for exportation were treated in Sicily, the annual output would amount to 3000 to 4000 tons of citric acid, which would suffice to supply the whole of Europe.

The French imports and exports are as follows (tons):

			1913	1914	1915	1916
Citric acid	Juice	imported	134	58	19	146
		exported	31	12	11	131
	Crystals	imported	29	58	37	95
		exported	452	249	272	207

In the West Indies the crude citrus materials produced corresponded with 1000 tons of calcium citrate in 1913 and with 1200 tons in 1914.

The Argentine imported 111 tons of citric acid in 1910 and 208 tons in 1911.

For Germany the imports and exports are as follows (tons):

	1902	1905	1909	1910	1911	1912	1913
Imports	306	—	193	206	178	162	310
Exports	163	379	358	381	553	550	528

In addition, 360 tons of lemon juice were imported into Germany in 1908 and 170 tons in 1909.

The *import duty* in Italy was formerly £4 per ton, but was raised in 1909 to £20 to protect a large factory, with £40,000 capital, erected in 1910–1911 near Palermo by the firm of Goldenberg; during the war this factory became solely Italian, with the title Fabbrica Chimica Arenella, and it now supplies Italian needs and is able to export a considerable quantity of citric acid (*see above*).

In Austria there are two citric acid factories, which, in 1906, imported 54 tons of calcium citrate from Sicily, 145 from Turkey, and 435 from Greece. France has two factories, these importing 1811 tons of Sicilian calcium citrate in 1906. In Germany there are nine citric acid works and four of pure citrates, 1318 tons of Sicilian calcium citrate being imported in 1908. In England there are ten works, almost all in London. The United States have three very large factories which produce more than 1000 tons of citric acid and import also a certain quantity from Europe, although the protective duty is £31 10*s.* per ton; calcium citrate, which is all imported (in 1911 about 2800 tons, of the value £160,000), is free from duty.

SALTS OF CITRIC ACID. Being tribasic, this acid forms three series of salts, as well as two different monosubstituted acids and two disubstituted acids. The alkali salts are all soluble in water, almost all of the others being insoluble, although dissolving in alkali citrates owing to the formation of double salts; in such solutions, the metals are no longer precipitable by ammonia, phosphates, or alkali carbonates. When heated, many citrates give salts of aconitic acid.

CALCIUM CITRATE, $(C_6H_5O_7)_2Ca_3 + 4H_2O$. If calcium hydroxide is added to a dilute solution of citric acid, no precipitate forms in the *cold* but one separates in the hot.

In presence of ammonia, calcium chloride gives no precipitate in the cold, while that formed in the hot partly dissolves on cooling but does not dissolve in caustic soda, and so differs from calcium tartrate (*see* p. 401). In moderately concentrated solutions, calcium chloride precipitates calcium citrate, although incompletely, even in the cold; in the hot, precipitation is complete. The water of crystallisation is wholly expelled at about 200°.

Calcium citrate is soluble in ammonium citrate with formation of a double salt precipitable by alcohol.

The manufacture and statistics of calcium citrate are considered above.

BARIUM CITRATE is less soluble in cold water than the calcium salt.

MAGNESIUM CITRATE, $(C_6H_5O_7)_2Mg_3$, is formed by dissolving magnesium carbonate in citric acid solution. It is used as a purgative and is then prepared by heating a mixture of 105 parts of powdered citric acid with 30 parts of magnesium oxide cautiously at 100° to 105°, pouring the fused mass on to porcelain tiles and powdering when cold. Large quantities of *effervescent magnesia* are prepared nowadays as a purgative and refreshing drink by mixing magnesium citrate with sodium bicarbonate and small proportions of citric acid and sugar, and granulating the mass with addition of a little glucose. Citric acid and, to some extent, magnesium citrate are often adulterated with tartaric acid, which is cheaper.

CITRATE OF IRON is obtained as a dark red colloidal solution by dissolving ferric hydroxide in cold citric acid solution. Such solutions of different concentrations give, on heating, various citrates of iron which are soluble in ammonium citrate and more or less soluble in water, and have been studied in recent years in relation to their colloidal character.

Of the **HIGHER POLYBASIC HYDROXY-ACIDS** the following may be mentioned: *Desoxalic acid,* $CO_2H \cdot CH(OH) \cdot C(OH)(CO_2H)_2$, which forms deliquescent crystals and, when boiled with water, loses CO_2 and gives uvic acid; *hydroxycitric acid* (dihydroxytricarballylic acid), $C_3H_3(OH)_2(CO_2H)_3$, found in the beet; *acetonetricarboxylic acid* and various acids which contain four, five, or even more carboxyl groups and are of synthetic and not of natural origin.

IV. THIO-ACIDS AND THIO-ANHYDRIDES

These may be regarded as acids or anhydrides in which an oxygen atom is replaced by sulphur, as in **THIOACETIC ACID** (Ethanthiolic Acid), $CH_3 \cdot CO \cdot SH$, which is obtained by the action of phosphorus pentasulphide on acetic acid and is a colourless liquid boiling below 100°, giving an odour of acetic acid and hydrogen sulphide; these two compounds are also formed by the action of water on the acid. **ETHANTHIOLTHIOLIC ACID,** $CH_3 \cdot CS \cdot SH$, is a dithio-acid, and **ACETYL SULPHIDE,** $(CH_3 \cdot CO)_2S$, a thio-anhydride. The esters corresponding with these acids, *e.g.*, **ETHYL THIOACETATE,** $CH_3 \cdot CO \cdot SC_2H_5$, a liquid boiling unchanged and yielding the acid and mercaptan on hydrolysis, are also known.

V. AMIDO-ACIDS, AMINO-ACIDS, IMIDES, AMIDINES, THIOAMIDES, IMINO-ETHERS, AND ANALOGOUS COMPOUNDS

A. AMIDO-ACIDS (AMIDES) AND DERIVATIVES

Like the amines (*see* p. 239), the amides may be regarded as derivatives of ammonia, the hydrogen atoms of which are replaced, not by alkyl, but by acid radicals.

There are thus *primary, secondary,* and *tertiary amides,* which are obtained by the replacement of one, two, or three atoms of hydrogen, and are sharply distinguished from the amines, as they are readily hydrolysed by alkali, acid, or superheated water, giving ammonia and the corresponding acids. They are generally crystalline substances soluble in alcohol or ether, and the lower members, especially of the primary amides, dissolve also in water. Their boiling-points are much higher than those of the corresponding amines.

Amides are also known in which one or two atoms of the ammoniacal hydrogen are replaced by alkyl radicals, *i. e.*, *alkylated amides*, *e. g.*, *ethylacetamide* or *acetylethylamine*, $CH_3 \cdot CO \cdot NH \cdot C_2H_5$, and *dimethylacetamide*, $CH_3 \cdot CO \cdot N(CH_3)_2$, from which, on hydrolysis, only the acid is separated, the alkyl residue or residues remaining joined to the amino-group, forming non-hydrolysable amines.

PREPARATION. (1) By dissolving an alkyl cyanide (nitrile) in concentrated sulphuric acid, either with or without concentrated acetic acid, concentrated hydrochloric acid or hydrogen peroxide, a molecule of water is added: $CH_3 \cdot CN + H_2O = CH_3 \cdot CO \cdot NH_2$. By heating acids or anhydrides with nitriles, secondary or tertiary amides are formed.

(2) The action of ammonia solution or solid ammonium carbonate on acid chlorides yields primary amides, whilst, if the ammonia is replaced by an amine, an alkylated amide is obtained:

$$CH_3 \cdot CO \cdot Cl + 2NH_3 = NH_4Cl + CH_3 \cdot CO \cdot NH_2$$

$$CH_3 \cdot CO \cdot Cl + 2NH_2 \cdot C_2H_5 = \underset{\text{Ethylamine hydrochloride}}{C_2H_5 \cdot NH_2, HCl} + \underset{\text{Ethylacetamide}}{CH_3 \cdot CO \cdot NH \cdot C_2H_5}.$$

On the other hand, the anhydrides give, with ammonia, the primary anhydride and an ammonium salt.

(3) By heating ammonium salts of the fatty acids in closed vessels at about 250°, primary amides are formed:

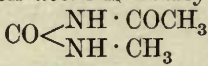
$$CH_3 \cdot CO_2NH_4 = H_2O + CH_3 \cdot CO \cdot NH_2.$$

PROPERTIES. Unlike the amines, the amides have only a very feeble basic character, owing to the presence of the negative acid radical, and only the primary ones give additive products with acids, *e. g.*, $CH_3 \cdot CO \cdot NH_2, HCl$, acetamide hydrochloride, which is decomposed even by water. Also certain sodium and mercuric derivatives are known, *e. g.*, $(CH_3 \cdot CO \cdot NH)_2Hg$, which exhibit the amides as feebly acid compounds, one of the hydrogen atoms of the amido-group being replaceable by metals.

With nitrous acid, amides react similarly to primary amines, giving the acid and liberating nitrogen:

$$CH_3 \cdot CO \cdot NH_2 + NO_2H = H_2O + N_2 + CH_3 \cdot CO_2H.$$

Removal of water from primary amides by means of phosphorus pentachloride or pentoxide results in the formation of alkyl cyanides (nitriles).

By the gradual action of bromine in presence of alkali, the corresponding amine with one less carbon atom is finally obtained, while urea derivatives, such as *methylacetylurea*,  $CO{<}\begin{smallmatrix}NH \cdot COCH_3\\ NH \cdot CH_3\end{smallmatrix}$, are formed as intermediate products, these being decomposable by excess of alkali; an intermediate bromo-compound, *e. g.*, *acetobromamide*, $CH_3 \cdot CO \cdot NHBr$, is also formed, this giving the amine with liberation of CO_2:

$$CH_3 \cdot CO \cdot NHBr + KOH = KBr + CO_2 + CH_3 \cdot NH_2.$$

When, however, the acid residue contains more than five carbon atoms, the nitrile is obtained instead of the amine, which is acted on by the bromine: $C_nH_{2n+1} \cdot CH_2 \cdot NBr_2 = 2HBr + C_nH_{2n+1} \cdot CN$. Since the nitriles may be converted into the acids containing one less carbon atom than the amides from which they originate, it is hence possible *to pass gradually from higher acids to more and more simple ones*.

The ready hydrolysability and the methods of formation of amides confirm their constitutional formula, $X \cdot CO \cdot NH_2$. With the alkali salts, however, the existence of the isomeric modification, $X \cdot C(OH) : NH$ (*see* Tautomerism, pp. 18 and 394) is assumed, but if the hydrogen of the hydroxyl or amino-group is replaced by an alkyl residue, no tautomeric forms occur, only true structural isomerides, $X \cdot CO \cdot NHR$ and $X \cdot C(OR) : NH$. The latter are termed *imino-ethers* and are derived from the hypothetical imino-hydroxides of the acids, *e. g.*, $CH_3 \cdot C(OH) : NH$. They are prepared by the action of a nitrile on an alcohol in presence of gaseous hydrogen chloride; thus, with HCN, the *hydrochloride of formiminic ether*, $CH(OC_2H_5) : NH$, is obtained as a white powder.

It is worthy of mention that Effront decomposes amino-acids on an industrial scale by means of special ferments so as to obtain fatty acids and ammonia from them (*see* pp. 183 and 348).

FORMAMIDE (Methanamide), $H \cdot CO \cdot NH_2$, prepared as described above, is a liquid which is soluble in water and alcohol, boils at 200° with partial decomposition, and gives ammonia and carbon monoxide when rapidly heated; with P_2O_5 it yields HCN, and with chloral, an additive product, *chloralamide*, which is used as an antiseptic and hypnotic.

ACETAMIDE (Ethanamide), $CH_3 \cdot CO \cdot NH_2$, forms needles melting at 82° and boils at 222°. *Diacetyl-derivatives* [1] are obtained less easily. *Diacetamide*, $(CH_3 \cdot CO)_2NH$, melts at 78°, boils at 223°, and is obtained by heating acetamide with acetic anhydride.

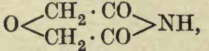
OXAMIC ACID, $CO_2H \cdot CO \cdot NH_2$, is the monamide of oxalic acid and is obtained as a white, crystalline powder, slightly soluble in cold water, when ammonium oxalate is heated.

OXAMIDE, $NH_2 \cdot CO \cdot CO \cdot NH_2$, is the diamide or normal amide of oxalic acid, and is obtained by the partial hydrolysis of cyanogen or by distillation of ammonium oxalate. In appearance it closely resembles oxamic acid and it is insoluble in water or alcohol and is readily hydrolysed; elimination of water (by P_2O_5) from it leads to cyanogen (*see* p. 240).

SUCCINAMIC ACID, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, is analogous to oxamic acid, and succinamide, $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, is prepared similarly to oxamide, to which it is analogous; succinamide crystallises from water in shining needles, and decomposes at 200° into ammonia and succinimide.

Of the *amides of hydroxy-acids*, only the following need be mentioned:

GLYCOLLAMIDE, $OH \cdot CH_2 \cdot CO \cdot NH_2$, which is obtained by treating the ester of glycollic acid with ammonia or, better, by heating ammonium tartronate at 150°, melts at 120° and has a sweet taste. The *diglycollamides*, $NH_2 \cdot CO \cdot CH_2 \cdot O \cdot CH_2 \cdot CO_2H$ and $(CH_2 \cdot CO \cdot NH_2)_2O$, are also known, the latter, on heating, giving ammonia and *diglycollimide*,



$O\left<\begin{matrix}CH_2 \cdot CO \\ CH_2 \cdot CO\end{matrix}\right>NH$, which melts at 142°.

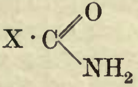
MALIC ACID, $CO_2H \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, forms two amides by means of its two carboxyl groups, an amine by means of its alcoholic group (aspartic acid), and also an amino-amide (asparagine).

MALAMIC ACID, $NH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, is known best as its crystalline ethyl ester, which is formed by the action of ammonia on an alcoholic solution of ethyl malonate.

MALAMIDE, $NH_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CO \cdot NH_2$, is formed by the action of ammonia on ethyl malonate in the dry state.

B. IMIDES AND IMINO-ETHERS

Attention must be drawn, not so much to the secondary amides [in which two hydrogen atoms of ammonia are replaced by two acid residues, *as in diacetamide*, $(CH_3 \cdot CO)_2NH$, which contains the iminic group, NH] or to the tautomeric form of the primary amides (with



corresponds the

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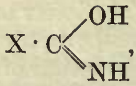
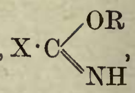
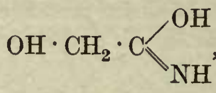
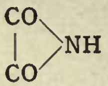
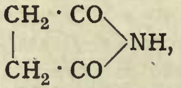
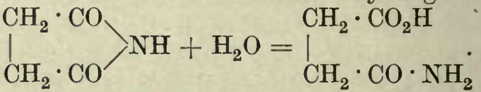
[1] In general, *diacetylamines* or *diacylamines* of the fatty or aromatic series are obtained by one of the following methods: (1) By heating isocyanic esters with acetic anhydride; (2) by the action of a current of HCl in the hot on the primary amides: $2CH_3 \cdot CO \cdot NH_2 + HCl = (CH_3 \cdot CO)_2NH + NH_4Cl$; part, however, undergoes decomposition: $(CH_3 \cdot CO)_2NH \rightleftarrows CH_3 \cdot CN + CH_3 \cdot CO_2H$; (3) from amines and acid chlorides, either with or without pyridine; (4) by heating nitriles with acids; (5) by heating amines with acetic anhydride in a sealed tube at 200°; from urea and acetic anhydride in the hot, etc., etc.

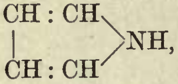
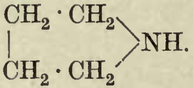
The melting-points of some *acylamines* are as follows: *butyramide*, 115°; *dibutyramide*, 107°; *isobutyramide*, 129°; *di-isobutyramide*, 174°; *propionamide*, 79°; *dipropionamide*, 153°.

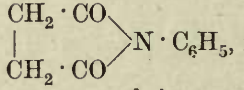
isomeride , which is well known in the form of *imino-ethers*, , or, in the case of the *imidohydrin of glycollic acid*, , in the free state) as to the imides of certain dibasic acids.

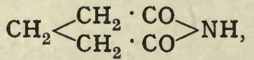
OXIMIDE,  (perhaps with the double formula), is formed on elimination of water from oxamic acid (by PCl_5).

SUCCINIMIDE, , is obtained by heating succinic anhydride in a current of ammonia or by heating the diamide or rapidly distilling mono-ammonium succinate, as has been mentioned on p. 365, where the reason was given for the ready formation of the closed-ring internal anhydrides.

Succinimide melts at 126° and boils at 288°, crystallises with $1H_2O$ and *exhibits the characters of an acid*, the iminic hydrogen, influenced by the two carboxyl groups, being replaceable by acids. On the other hand, when they are treated with alkali, these imides give the amides from which they originate, a molecule of water being added: .

It is interesting that, when succinimide is distilled over zinc dust, it yields *pyrrole*, , while, if it is heated in alcoholic solution with sodium (reduction), it gives **Pyrrolidine**, .

Also **Phenylsuccinimide (Succinanil)**, , is known and its various transformations confirm the symmetry of its own structure and consequently also that of succinimide.

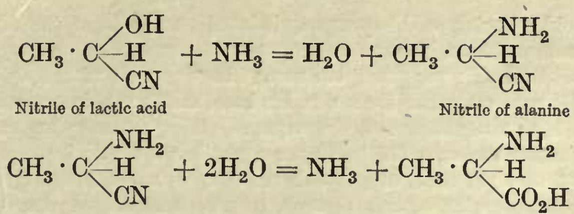
GLUTARIMIDE, , is obtained by distilling ammonium glutarate; it melts at 152° and gives a little pyridine when heated with zinc dust.

C. AMINO-ACIDS AND THEIR DERIVATIVES

In the amino-acids, it is the hydrogen in direct union with carbon that is replaced by the NH_2-group, the carboxyl group remaining intact, so that these compounds have both acidic and basic functions, and may hence be readily separated from other substances, since after the carboxyl is esterified, salts such as the hydrochlorides of the amino-group are formed.

These substances and their derivatives are of considerable importance in animal and vegetable physiology, since they are found among the products of the gradual synthesis and decomposition of the proteins in the living organism; they are also of interest theoretically, as they form intermediate products in various chemical syntheses.

The *a*-amino-acids are readily obtained by the action of ammonia on the cyanohydrins of ketones and aldehydes and hydrolysis of the remaining nitrile group:



Nitrile of lactic acid

Nitrile of alanine

Alanine (α-Aminopropionic acid)

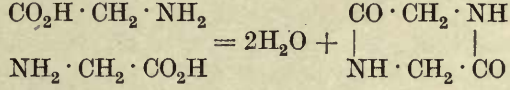
They are also formed generally by reducing the oximes of ketonic acids or, better, by the action of ammonia on halogenated acids:

$$CO_2H \cdot CH_2Cl + NH_3 = HCl + CO_2H \cdot CH_2 \cdot NH_2.$$

We may also mention the interesting Körner-Menozzi reaction (*see note*, p. 375), which allowed these authors, by inverting the reaction, to pass from the esters of unsaturated acids (fumaroid or maleinoid form) to a single form of the corresponding saturated amino-acids by simple treatment with ammonia (or even an alkylamine in alcoholic solution).

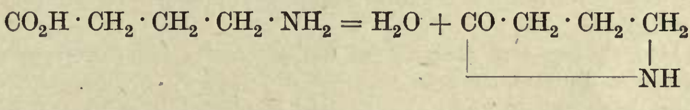
PROPERTIES. With nitrous acid, the amino-acids give hydroxy-acids with elimination of nitrogen, and they give many reactions analogous to those of the hydroxy-acids and varying with the position of the amino-group.

Two molecules of an α-amino-acid readily lose 2 mols. of water, giving a kind of anhydride with an imido-ketonic character:



$$\begin{array}{l} CO_2H \cdot CH_2 \cdot NH_2 \\ NH_2 \cdot CH_2 \cdot CO_2H \end{array} = 2H_2O + \begin{array}{|l|} CO \cdot CH_2 \cdot NH \\ NH \cdot CH_2 \cdot CO \end{array}$$

The γ-amino-acids, however, give internal anhydrides analogous to the lactones and termed **Lactams**:



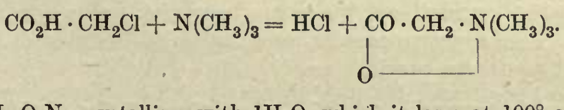
$$CO_2H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2 = H_2O + \begin{array}{|l} CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \\ \underline{\qquad\qquad\qquad} NH \end{array}$$

The β-amino-acids, when heated, evolve ammonia and give unsaturated acids.

The amino-acids resist the action of boiling alkali solutions, but when fused with caustic soda they yield the sodium salts of the monobasic acids, ammonia being liberated. On dry distillation (best in presence of baryta) they yield amines and CO_2, *e. g.*, $CH_3 \cdot CH(NH_2) \cdot CO_2H = CH_3 \cdot CH_2 \cdot NH_2 + CO_2$.

The stereoisomerides may be separated by means of the strychnine or brucine salts, etc.

GLYCOCOLL (Glycine, Aminoacetic or Aminoethanoic Acid, or Amine of Glycollic Acid), $CO_2H \cdot CH_2 \cdot NH_2$, is formed on boiling gelatine with alkali [$Ba(OH)_2$] or acid (dilute H_2SO_4) or on heating *hippuric acid* (benzoylglycocoll) with dilute acid: $CO_2H \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_5 + H_2O = CO_2H \cdot CH_2 \cdot NH_2 + C_6H_5 \cdot CO_2H$ (benzoic acid). Synthetically it is obtained from monochloracetic acid and concentrated ammonia (*see* p. 385); if the ammonia is replaced by methylamine, *sarcosine*, $CO_2H \cdot CH_2 \cdot NH \cdot CH_3$, m.-pt. 115°, is obtained, or if by trimethylamine, betaine (*see* p. 385) is formed:



$$CO_2H \cdot CH_2Cl + N(CH_3)_3 = HCl + \begin{array}{|l|} CO \cdot CH_2 \cdot N(CH_3)_3. \\ O \end{array}$$

Betaine, $C_5H_{11}O_2N$, crystallises with $1H_2O$, which it loses at 100° or in a desiccator over sulphuric acid. It dissolves in water or alcohol, from which it is precipitated by ether, or as *betaine hydrochloride* by hydrochloric acid. This solid hydrochloride is soluble in water, which hydrolyses it to a considerable extent, the solution then behaving like hydrochloric acid. Owing to this property it is sold, under the name of *acidol*, in pastilles containing exact and suitable doses for stomach complaints, and replaces solutions of hydrochloric acid for this purpose; the same effect as that of the acid is thus obtained by use of a solid product. *Betaine* is a feeble base, and is not decomposed even by boiling *aqua regia;* at high temperatures it decomposes, giving trimethylamine. It occurs abundantly in beet-sugar molasses (10 to 12 per cent., besides 1 to 2 per cent. of *leucine* and *isoleucine* and 5 to 7 per cent. of *glutamic acid*), from which it is extracted by means of alcohol; after evaporation of this solvent, it is separated as hydrochloride.

The action of tertiary amines, other than trimethylamine, with monochloracetic acid gives various compounds to which is given the name of **BETAINES.**

Substitution in the amino-group of the amino-acids also yields other interesting compounds, *e. g.*, **Aceturic Acid** (*acetylglycocoll*), $CO_2H \cdot CH_2 \cdot NH \cdot CO \cdot CH_3$, melting at 206°.

The properties of glycocoll and its salts are given on p. 385.

In the amino-acid group is also found **SERINE** or α-amino-β-hydroxypropionic acid, $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot OH$, which is obtained on boiling silk gelatine with dilute sulphuric acid or synthetically from glycollic aldehyde, ammonia, and hydrocyanic acid. **LEUCINE** (α-aminoisocaproic acid), $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CH(CH_3)_2$, is obtained synthetically by hydrolysing the nitrile of isovaleraldehyde-ammonia, and is usually found with glycine among the products of decomposition of the proteins by acid or alkali, and is then optically active (the carbon atom adjacent to the carboxyl being asymmetric).

ASPARTIC ACID (**Aminosuccinic Acid**), $CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, is one of the most important products obtained by the decomposition of proteins by acid or alkali. It occurs in abundance (lævo-rotatory) in beet-sugar molasses, and has been prepared by various synthetic methods, *e. g.*, by the action of ammonia on bromosuccinic acid.

Three stereoisomerides are known, two of them being optically active owing to the presence of an asymmetric carbon atom. They are obtained in small, tabular, dimetric crystals, soluble to some extent in hot water. Their cold solutions and also acid solutions of the dextro-rotatory acid have a sweet taste, but hot solutions or alkaline solutions of the lævo-rotatory acid are without taste.

They give the general reaction of amines and amides with nitrous acid, being converted into malic acid.[1]

The higher homologue of aspartic acid is **Glutamic Acid** (*a-aminoglutaric acid*), $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

Among the **DIAMINO-ACIDS** we have **Lysine**, $CO_2H \cdot CH(NH_2) \cdot [CH_2]_4 \cdot NH_2$, which is obtained by the action of acids on proteins or by synthetical methods; on putrefaction it gives pentamethylenediamine.

Ornithine, $CO_2H \cdot CH(NH_2) \cdot [CH_2]_3 \cdot NH_2$, is the lower homologue of lysine and gives tetramethylenediamine (*putrescine*) on putrefaction.

Taurine (*Ethyleneaminosulphonic Acid*), $SO_3H \cdot CH_2 \cdot CH_2 \cdot NH_2$, is found in ox-bile combined with cholic acids as *taurocholic acid* (for properties of taurine, *see* p. 257).

Cysteine (*Thioserine*), $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot SH$, is formed by the reduction of cystine, $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, which occurs in urinary sediments (calculi).

ASPARAGINE, $NH_2 \cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, is the amide of aspartic acid. It was first found in asparagus, but is moderately widespread in almost all vegetables (beet, potatoes, beans, vetches, peas, etc.), especially during the germination period, and the dry seeds of certain lupins contain as much as 30 per cent. The constitution of asparagine is confirmed by the various syntheses leading to its production.

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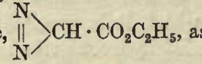
[1] By the action of nitrous acid on the ethyl ester of glycocoll, Curtius obtained **Ethyl Diazoacetate**,



$\begin{matrix} N \\ \| \\ N \end{matrix} \!\!>\! CH \cdot CO_2C_2H_5$, as a yellow oil with a peculiar odour; when heated it explodes, while with water it loses nitrogen and forms ethyl glycollate.

It crystallises with $1H_2O$ in lævo-hemihedral, trimetric prisms, soluble in hot water but insoluble in alcohol or ether.

With aqueous cupric acetate solution, it forms a blue, well-crystallised copper salt, $(C_4H_7O_3N_2)_2Cu$, insoluble in water. It is isomeric with malamide, from which it differs in the possession of both acid and basic characters. It is lævo-rotatory and has an unpleasant, insipid taste, but vetch seedlings contain a dextro-rotatory asparagine which has a sweet taste (Piutti, 1886), but does not unite with the lævo-rotatory form—also present in the seedlings —to give the inactive modification. Pasteur stated that the substance composing the nerves of the palate behaves as an optically active combination which acts differently towards the dextro- and lævo- asparagines.

Asparagine is converted into aspartic acid by hydrolysis and into malic acid by the action of nitrous acid.

ASPARTAMIDE, $NH_2 \cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH_2$, is the diamide or normal amide of aspartic acid.

Numerous higher homologues of aspartic acid (Homo-Aspartic Acids) and of asparagine (Homo-Asparagines) are known.

D. AMIDO- AND IMIDO-CHLORIDES

With both the primary amides and also the alkylated amides, the oxygen is readily replaced by chlorine by the action of PCl_5. Thus, acetamide gives *acetamido-chloride*, $CH_3 \cdot CCl_2 \cdot NH_2$, and ethylacetamide, *ethylacetamido-chloride*, $CH_3 \cdot CCl_2 \cdot NH \cdot C_2H_5$. Both of these compounds readily lose HCl, forming *imino-chlorides, e. g., acetimino-chloride*, $CH_3 \cdot CCl : NH$, and *ethylacetimino-chloride*, $CH_3 \cdot CCl : N{\cdot}C_2H_5$. These imino-chlorides, like amido-chlorides, are readily decomposed by water into hydrogen chloride and amide. These chlorinated compounds react easily with aromatic substances and with hydrogen sulphide, ammonia, and amines, the chlorine being thus replaced by sulphur or by amino-residues, forming *thioamides, e. g.*, $CH_3 \cdot CS \cdot NHX$, and *amidines, e. g.*, $CH_3 \cdot C(NH_2) : NX_2$.

E. THIOAMIDES

These are well-crystallised compounds, more acid in character than the amides, and hence capable of forming metallic derivatives and of dissolving in alkali. Besides by the reaction just mentioned they are obtained by the addition of H_2S to nitriles: $CH_3 \cdot CN + H_2S = CH_3 \cdot CS \cdot NH_2$ (*thioacetamide* or *ethanethioamide*); on heating, the opposite change occurs.

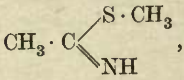
Phosphorus pentasulphide replaces the oxygen of amides by sulphur, thus forming thioamides. With H_2S, isonitriles give the alkylated thioamides of formic acid, $CN \cdot X + H_2S = H \cdot CS \cdot NHX$.

Thioamides are readily hydrolysed (by alkali, hot water, etc.), with formation of H_2S, NH_3 (or amine), and the corresponding acids:

$$X \cdot CS \cdot NHX' + 2H_2O = X \cdot CO_2H + NH_2X' + H_2S.$$

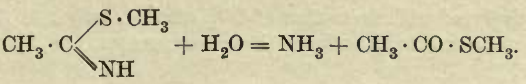
F. IMINOTHIOETHERS

The thioamides (and especially their derivatives) can exist in the isomeric or tautomeric form, $X \cdot C(SH) : NH$, in which the hydrogens of both the sulphydryl and the imino-group are replaceable by alkyl groups, Iminothioethers, *e. g.*, $X \cdot C(SX') : NH$, being then formed. These are prepared by the action of alkyl iodides on the thioamides (also from thioalcohols, nitriles, and gaseous hydrogen chloride), *e. g.*, $CH_3 \cdot CS \cdot NH_2 + CH_3I =$



$CH_3 \cdot C\left\langle\begin{matrix} S \cdot CH_3 \\ NH \end{matrix}\right.$, HI (*acetiminothiomethyl hydriodide*).

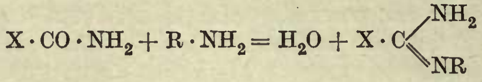
The iminothioethers are easily hydrolysed (by HCl), forming ammonia and esters of thio-acids;



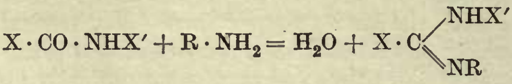
$$CH_3 \cdot C\left\langle\begin{matrix} S \cdot CH_3 \\ NH \end{matrix}\right. + H_2O = NH_3 + CH_3 \cdot CO \cdot SCH_3.$$

G. AMIDINES

When the amides or alkylamides are heated with amines in presence of a dehydrating agent (like PCl_3), the oxygen of the amide is substituted by an imino-residue:

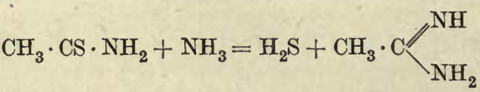


$$X\cdot CO\cdot NH_2 + R\cdot NH_2 = H_2O + X\cdot C\left\langle\begin{matrix}NH_2\\NR\end{matrix}\right.$$

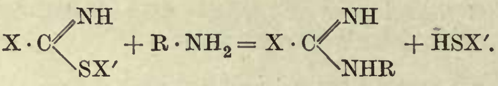


$$X\cdot CO\cdot NHX' + R\cdot NH_2 = H_2O + X\cdot C\left\langle\begin{matrix}NHX'\\NR\end{matrix}\right.$$

These compounds are obtained also from thioamides, isothioamides, iminochlorides, or iminoethers by the action of ammonia or of primary or secondary amines:



$$CH_3\cdot CS\cdot NH_2 + NH_3 = H_2S + CH_3\cdot C\left\langle\begin{matrix}NH\\NH_2\end{matrix}\right.$$ (*acetamidine* or *ethanamidine*).

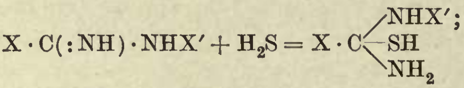


$$X\cdot C\left\langle\begin{matrix}NH\\SX'\end{matrix}\right. + R\cdot NH_2 = X\cdot C\left\langle\begin{matrix}NH\\NHR\end{matrix}\right. + HSX'.$$

When nitriles are heated with the hydrochlorides of primary (of the aromatic series also) or secondary amines (not with NH_4Cl), alkylamidines are obtained:

$$CH_3\cdot CN + R\cdot NH_2 = CH_3\cdot C(:NH)\cdot NHR.$$

Properties. The amidines (or *amimides*) are bases and usually of the aromatic series; they are easily hydrolysed (by boiling with alkali or acid), giving (when the iminic hydrogen is not replaced by an alkyl group) ammonia (or an amine) and a nitrile; the same change occurs on dry distillation. With H_2S they give first an additive product:



$$X\cdot C(:NH)\cdot NHX' + H_2S = X\cdot C\left\langle\begin{matrix}NHX'\\SH\\NH_2\end{matrix}\right.;$$

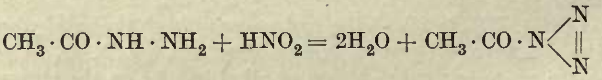
this product then decomposes in two senses, giving (*a*) $X\cdot CS\cdot NHX' + NH_3$ and (*b*) $X\cdot CS\cdot NH_2 + X'\cdot NH_2$.

With CS_2, amidines give thioamides and, at the same time, thiocyanic acid or an alkyl thiocyanate.

H. HYDRAZIDES AND AZIDES

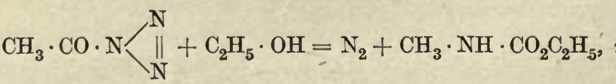
Introduction of an acid residue into hydrazine, $H_2N\cdot NH_2$ (*see* Vol. I., p. 376), gives the *primary hydrazides* or *monoacylhydrazides, e. g.,* $CH_3\cdot CO\cdot NH\cdot NH_2$ (*acetylhydrazide*) and $H\cdot CO\cdot NH\cdot NH_2$ (*formhydrazide,* m.-pt. 54°); two acid radicals give *secondary hydrazides* or *dihydrazides, e. g.,* $CH_3\cdot CO\cdot NH\cdot NH\cdot CO\cdot CH_3$ (*diacethydrazide,* which melts at 138° and is prepared from hydrazine hydrate and acetic anhydride).

They are readily hydrolysable, and reduce ammoniacal silver nitrate solution in the cold and Fehling's solution on heating. The primary hydrazides are more highly basic than the amides, and so give more stable salts. Nitrous acid acts on primary hydrazides, forming *azides,* which are derivatives of hydrazoic acid (*see* Vol. I., p. 376):



$$CH_3\cdot CO\cdot NH\cdot NH_2 + HNO_2 = 2H_2O + CH_3\cdot CO\cdot N\left\langle\begin{matrix}N\\\|\\N\end{matrix}\right.$$

These resemble the acichlorides in many properties, but are explosive (silver and lead azides, *see* p. 310) and, when heated with alcohol, give urethanes and liberate nitrogen:



$$CH_3\cdot CO\cdot N\left\langle\begin{matrix}N\\\|\\N\end{matrix}\right. + C_2H_5\cdot OH = N_2 + CH_3\cdot NH\cdot CO_2C_2H_5,$$ *methylurethane,*

which may be hydrolysed with formation of CO_2, alcohol, and methylamine. It is hence possible to pass from an acid to an amine with one carbon atom less, by way of the hydrazide and azide.

I. HYDROXYLAMINE-DERIVATIVES OF ACIDS

Hydroxylamine or its residues may be united to acid residues, forming **Hydroximic** (or *hydroxamic*) **Acids**, *e.g.*, $CH_3 \cdot C(:N \cdot OH)OH$ (*ethylhydroxamic acid*, m.-pt. 59°), and **Amidoximes**, $X \cdot C(:N \cdot OH) \cdot NH_2$. The hydroxamic acids have an acid character and are formed, with evolution of ammonia, by the action of hydroxylamine on amides.

Also **Formyloxime Chloride**, $CH(:N \cdot OH)Cl$, is known, this being obtained by treating mercury fulminate in the cold with HCl; it forms needles, which are readily decomposable, volatile, and soluble in ether.

The Amidoximes are formed by the addition of nitriles to hydroxylamine, $CH_3CN + NH_2 \cdot OH = CH_3 \cdot C(:NOH)NH_2$. If hydrogen cyanide is employed, **ISURET** (Methanamidoxime or Methenylamidoxime), $CH(:NOH)NH_2$, isomeric with urea, would be obtained.

VI. CYANOGEN COMPOUNDS

Some cyanogen compounds, especially **Hydrocyanic Acid**, HCN, **potassium cyanide**, and **ferro-** and **ferri-cyanides**, have already been dealt with in Vol. I., pp. 497, 547, and 840. We have to consider here the numerous and varied organic derivatives of cyanogen, which are of some interest as they often exist in polymerised forms and almost always in two isomeric modifications, sharply differentiated by their chemical properties: derivatives of *nitriles*, $X \cdot C \vdots N$, and of *isonitriles*, $C \,\vdots\, N \cdot X$ (*see also* p. 237).

CYANOGEN, $(CN)_2$, is a highly poisonous gas with a pungent odour recalling that of bitter almonds; it is liquid at − 21° and solid at − 34°. It is found in the gas from blast-furnaces and occurs largely in the tail of Halley's comet, which approached the earth in May 1910. It is obtained by the elimination of water from ammonium oxalate or oxamide ($NH_2 \cdot CO \cdot CO \cdot NH_2$) by the action of P_2O_5 in the hot, or by heating a solution of copper sulphate with potassium cyanide, and is commonly prepared by heating cyanide of silver or of mercury, $Hg(CN)_2 = Hg + (CN)_2$; as a secondary product, **PARACYANOGEN**, $(C_3N_3)_2$, or $(CN)_x$, is formed as a brown powder.

It burns with a purple flame, dissolves readily in alcohol or water (4 : 1), and its solutions gradually become brown, with formation of oxalic acid, formic acid, hydrocyanic acid, ammonia, and urea, and deposition of **Azulmic Acid** (brown powder). With H_2S it forms the thioamides: **RUBEANHYDRIC ACID**, $NH_2 \cdot CS \cdot CS \cdot NH_2$, and **FLAVEANHYDRIC ACID**, $NC \cdot CS \cdot NH_2$.

CYANOGEN CHLORIDE, $NC \cdot Cl$, is of importance in the synthesis of many cyanogen compounds, and is formed by the action of chlorine on hydrocyanic acid or metallic cyanides: $NC \cdot H + Cl_2 = HCl + NC \cdot Cl$. It is a colourless gas which is easily liquefied, boils at 15·5°, has a pungent odour, and dissolves in water. In presence of HCl it polymerises, forming **Cyanogen Trichloride** (melts at 145°, boils at 190°). With KOH it forms potassium cyanate, NCOK.

CYANIC ACID, $NC \cdot OH$, is a liquid of penetrating odour and only slight stability, even at the ordinary temperature.

It is obtained by the dry distillation of cyanuric acid (*q. v.*) and condensation of the vapours in a freezing mixture. It undergoes change, even at the ordinary temperature and with slight explosions, into a compact, white isomeride, which is polymerised *iso-cyanic acid* or *cyamelide*, $(O:C:NH)_x$; this, on dry distillation, gives cyanic acid again.

Its salts are more stable, but when attempts are made to liberate the acid from these by the action of mineral acids, immediate hydrolysis occurs:

$$NC \cdot OH + H_2O = CO_2 + NH_3.$$

If it is liberated by dilute acetic acid, the isomeric cyanuric acid is obtained.

The alkyl derivatives of cyanic acid exhibit two isomeric forms: **Cyanates**, $N \vdots C \cdot OX$, and **Isocyanates**, $O:C:NX$.

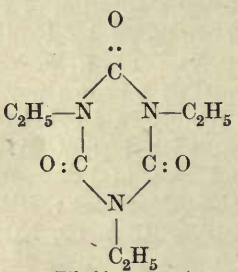
Potassium Cyanate, NCOK, forms white scales soluble in alcohol or water, and is obtained by oxidising solutions of potassium cyanide by means of potassium permanganate or dichromate, or by fusing potassium cyanide or ferrocyanide with PbO_2 or MnO_2: $NCK + O = NCOK$.

Ammonium Cyanate, $NC \cdot ONH_4$, is isomeric with urea, into which it can be converted. It is obtained by neutralising cyanic acid with ammonia and forms a moderately stable, white, crystalline mass.

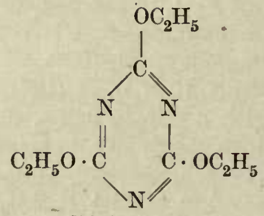
ETHYL ISOCYANATE, $CO : NC_2H_5$, is prepared by distilling potassium cyanate with either potassium ethyl sulphate or ethyl iodide. It is a liquid of penetrating odour and boils at 60°. It does not behave as a true ester (true esters of cyanic acid do not exist), since the action of acid or alkali yields, not alcohol, but ethylamine; $CO : NC_2H_5 + H_2O = CO_2 + C_2H_5 \cdot NH_2$. Hence the nitrogen is united directly to the alkyl group, so that the structure is not $N \vdots C \cdot OC_2H_5$, but $O : C : NC_2H_5$.

Ethyl isocyanate is instantly decomposed by water, forming derivatives of urea; the latter are also formed by the action of ammonia or amino-bases.

CYANURIC ACID, $(NC)_3(OH)_3$, is a polymeride of cyanic acid and on heating urea —which contains the constituents of ammonia and cyanic acid—either alone or in a current of chlorine so as to eliminate the elements of ammonia, there remain those of cyanic acid, which polymerise to cyanuric acid. It crystallises with $2H_2O$ in prisms, effloresces in the air, and is readily soluble in hot water. When heated with HCl, it hydrolyses slowly to NH_3 and CO_2; with PCl_5 it gives the chloride of cyanuric acid. It is a tribasic acid and forms a violet, crystalline copper salt; its sodium salt is insoluble in concentrated alkalis. Like cyanic acid, it gives rise to two series of derivatives, *e. g.*, **Ethyl Cyanurate**, $(NC)_3(OC_2H_5)_3$, which is a colourless liquid giving alcohol on hydrolysis. It is only slightly stable, and is readily transformed into the isomeride of the other series, **Ethyl Isocyanurate**, $(CO)_3(NC_2H_5)_3$, which is formed by polymerisation of ethyl isocyanate, or by distilling the cyanurate with potassium ethyl sulphate. On hydrolysis it gives ethylamine, this confirming its constitution, which is shown by the following closed-ring formulæ to be clearly different from that of ethyl cyanurate.

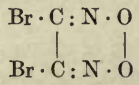


Ethyl isocyanurate



Ethyl cyanurate

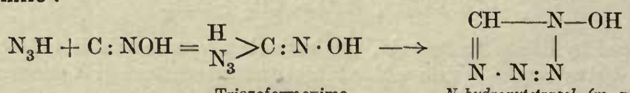
FULMINIC ACID, $C : NOH$, is readily volatile but unstable, and is decomposed by concentrated hydrochloric acid into hydroxylamine and formic acid, chloroformyloxime, $CHCl : N \cdot OH$, being formed as intermediate product. Kekulé regarded fulminic acid as a nitroacetonitrile, $NO_2 \cdot CH_2 \cdot CN$, but Nef subsequently attributed to it the constitution $C : N \cdot OH$, the carbon being divalent. With bromine, mercury fulminate (*see* p. 308) gives the compound



$$\begin{array}{l} Br \cdot C : N \cdot O \\ \quad\;\; | \qquad\;\; | \\ Br \cdot C : N \cdot O \end{array}$$

Silver fulminate is even more explosive than the mercury salt.

Palazzo (1907–1910) has prepared various additive products of fulminic acid with different acids (HBr, HI, $HSCN$, HNO_2, N_3H). With hydrazoic acid at − 12°, he obtained two isomerides with different constitutions, probably with intermediate formation of **Triazoformoxime**:

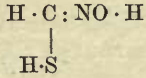


Triazoformoxime

N-hydroxytetrazole (m.-pt. 145°)

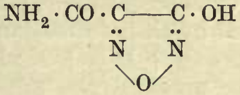
The other isomeride also is possibly a tetrazole derivative.

By the action of hydrogen sulphide on mercury fulminate suspended in water, Cambi (1910) obtained and isolated the Formothiohydroxamic Acid predicted by Nef:



$$\begin{array}{l} H\cdot C:NO\cdot H \\ \ \ \ \ | \\ H\cdot S \end{array}$$

FULMINURIC ACID, $C_3H_3O_3N_3$, is isomeric with cyanuric acid (*see above*), and two true isomerides are described: (1) *a-Isofulminuric acid*, obtained in 1884 by Ehrenberg by treating mercury fulminate suspended in ether first with gaseous hydrogen chloride and afterwards with concentrated ammonia solution, is infusible, and insoluble in water or alcohol, and gives a deep red coloration with ferric chloride; (2) *β-isofulminuric acid*, obtained in 1884 by Scholvien, melts at 196°. Ulpiani (1912) maintains the existence of only one fulminuric acid, to which he attributes the formula:



THIOCYANIC ACID AND ITS DERIVATIVES

THIOCYANIC ACID (Rhodanic Acid), $NC\cdot SH$, is a yellow liquid of penetrating odour, stable only when anhydrous in a freezing mixture or when in very dilute aqueous solution. At ordinary temperatures it polymerises to a yellow mass. It is obtained from its mercury salt (*see later*) by the action of hydrochloric acid.

In concentrated aqueous solution, it undergoes conversion into a yellow crystalline mass of Perthiocyanic Acid, $(CN)_2S_3H_2$.

Cyanogen Sulphide, $(NC)_2S$, may be regarded as a kind of anhydride of thiocyanic acid, and is obtained from silver thiocyanate and cyanogen iodide. It forms colourless plates which have a pungent odour and are readily soluble in water.

Thiocyanuric Acid, $(NC)_3(SH)_3$, is polymeric with thiocyanic acid, and is obtained by the action of sodium sulphide on cyanogen chloride. It is a yellow powder and gives salts corresponding with a tribasic acid. Its trimethyl salt is formed by polymerisation of ethyl thiocyanate by heating at 180°.

POTASSIUM THIOCYANATE (or Rhodanate), $NC\cdot SK$, *see* Vol. I., p. 841.

AMMONIUM THIOCYANATE (or Rhodanate), $NC\cdot SNH_4$, forms colourless, tabular crystals soluble in alcohol, and readily so in water. It is obtained by heating together CS_2 and NH_3 (*see also* Vol. I., p. 841). When heated it is transformed into the isomeric thiourea. It serves for the preparation of other thiocyanates, and is extracted in large quantities from the exhausted Laming mixture of gasworks (*see* p. 49), which contains 1 to 4 per cent. of it.

MERCURIC THIOCYANATE, $(NC\cdot S)_2Hg$, is prepared from a mercuric salt and ammonium thiocyanate, and forms a white, insoluble powder which swells up to a very considerable extent when heated (*Pharaoh's serpents*).

SILVER THIOCYANATE is precipitated as a white mass on mixing silver nitrate and ammonium thiocyanate. The latter gives, with ferric salts, a dark red coloration of **FERRIC THIOCYANATE** (sensitive indicator in the titration of silver with thiocyanate) and this, with potassium thiocyanate, gives a violet double salt, $(NC\cdot S)_6FeK_3$.

Hydrogen sulphide decomposes the thiocyanates, $NC\cdot SH + H_2S = NH_3 + CS_2$, while with concentrated sulphuric acid, addition of water and decomposition into ammonia and carbon oxysulphide occur

$$NC\cdot SH + H_2O = COS + NH_3.$$

For thiocyanic acid there are two series of isomeric derivatives, corresponding with the two general formulæ: $N\,\vdots\,C\cdot SX$ (alkyl thiocyanate) and $S:C:N\cdot X$ (mustard oils).

ETHYL THIOCYANATE, $NC\cdot SC_2H_5$, is a colourless liquid with a marked odour of garlic; it boils at 142° and is very slightly soluble in water. It is formed by the action of cyanogen chloride on mercaptides, or by distillation of potassium thiocyanate with potassium ethyl sulphate. As it has the constitution of a true ester, it is hydrolysed by alcoholic potash with formation of alcohol and potassium thiocyanate, but in certain reactions it behaves like the isomeric mustard oils. Nascent hydrogen converts it into mercaptan, since the alkyl is united to sulphur, and the action of nitric acid in the hot yields ethylsulphonic acid.

ALLYL THIOCYANATE, $NC \cdot SC_3H_5$, boils at 161°, and has a garlic-like odour; it undergoes change into the isomeric mustard oil, slowly at the ordinary temperature and more rapidly on distillation.

The **Mustard Oils (Isothiocyanates)** are obtained from the corresponding thiocyanates simply by heating. They are also formed by the action of carbon disulphide on the corresponding primary amines, $CS_2 + X \cdot NH_2 = H_2S + S : C : NX$, this change taking place by way of the intermediate alkylamine salt of alkyldithiocarbamic acid (*see later*), which is distilled with mercuric chloride. Mustard oils are formed also when an alkylated thiourea is distilled with phosphoric or concentrated hydrochloric acid.

Their structure is indicated by their formation of primary amine on hydrolysis :—$S : C : NX + 2H_2O = CO_2 + H_2S + X \cdot NH_2$. The isothiocyanic acid, $S : C : NH$, from which these mustard oils are regarded as derived, is not known in the free state.

METHYL MUSTARD OIL (Methyl Isothiocyanate), $SC : NCH_3$, melting at 34° and boiling at 119°; **Ethyl Mustard Oil**, $SC : NC_2H_5$, boiling at 134°; and **Propyl Mustard Oil**, $SC : NC_3H_7$, boiling at 153°, are of little importance. More interesting is

ALLYL MUSTARD OIL (or **Ordinary Mustard Oil ; Allyl Isothiocyanate**), $S : C : NC_3H_5$, which is prepared by distilling *Sinapis nigra* (*black mustard*) with water; it is obtained synthetically by the reactions given above. It is a liquid with a pungent odour recalling that of mustard and raises blisters on the skin; it is sparingly soluble in water and boils at 150·7°.

CYANAMIDE AND ITS DERIVATIVES

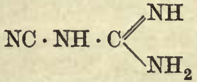
CYANAMIDE, $NC \cdot NH_2$, is a white crystalline substance, melting at 40° and dissolving very slightly in water, alcohol, or ether. It is obtained by passing a current of cyanogen chloride into an ethereal solution of ammonia: $2NH_3 + NC \cdot Cl = NH_4Cl + NC \cdot NH_2$, and is also formed by desulphurising thiourea, $NH_2 \cdot CS \cdot NH_2$, by means of HgO, which removes H_2S.

It is obtained abundantly and in a pure state by extracting calcium cyanamide (*see later*) systematically with water, neutralising the saturated solution with sulphuric acid, filtering from the calcium sulphate, concentrating in a vacuum, again filtering from the gypsum, concentrating anew, and extracting the crystalline mass—formed on cooling—with ether, which does not dissolve gypsum, dicyanamide, and other impurities. Evaporation of the ether yields pure cyanamide in almost theoretical yield (Baum, 1910).

With lapse of time, or rapidly at 150°, cyanamide changes into the polymeric dicyanodiamide (*see later*). It behaves both as a weak base forming unstable crystalline salts and as a weak acid giving metallic salts, *e.g.*, $NC \cdot NHNa$, $NC \cdot NAg_2$, etc. The most important of these is **calcium cyanamide**, $NC \cdot NCa$, which was considered in detail in Vol. I, pp. 369 *et seq.*, in the discussion of the utilisation of atmospheric nitrogen; it is formed by the action of nitrogen on heated calcium carbide and forms an excellent nitrogenous fertiliser.

In presence of dilute acid, cyanamide fixes a molecule of water, giving urea: $NC \cdot NH_2 + H_2O = NH_2 \cdot CO \cdot NH_2$; with hydrogen sulphide it yields thiourea. Cyanamide also gives two series of isomeric alkyl derivatives of the general formulæ, $N \vdots C \cdot NX_2$ and $XN : C : NX$. Compounds of the latter formula are derived from the hypothetical *carbodi-imide*, $NH : C : NH$; for example, *carbodiphenylimide*, $C_6H_5N : C : NC_6H_5$, boiling at 330°, is well characterised.

DIETHYLCYANAMIDE, $NC \cdot N(C_2H_5)_2$, is formed by the action of ethyl iodide on the silver salt of cyanamide, its structure being indicated by the products—$CO_2 + NH_3 + NH(C_2H_5)_2$—obtained on hydrolysis with dilute acid. *Methyl-* and *ethyl-cyanamide* are also known.

DICYANODIAMIDE, $(NC \cdot NH_2)_2$, is formed, as has already been mentioned, from cyanamide; certain of its reactions indicate the structure  $NC \cdot NH \cdot C\genfrac{}{}{0pt}{}{\diagup NH}{\diagdown NH_2}$ (Bamberger). It forms acicular crystals or small flat prisms. When heated strongly and rapidly, it is converted into a white insoluble powder, **MELAM**, $C_6H_9N_{11}$ or $[(NC)_3(NH_2)_2]_2NH$, this being an imide of melamine, into which it is transformed by sulphuric acid or ammonia.

MELAMINE (Cyanurtriamide), $(NC)_3(NH_2)_3$, is a crystalline basic substance, insoluble in alcohol or ether. When it is boiled with acid, the amino-groups are gradually replaced by hydroxyl groups, giving **AMMELINE**, $(NC)_3(NH_2)_2OH$, then **AMMELIDE**, $(NC)_3NH_2(OH)_2$, and finally Cyanuric Acid, $(NC)_3(OH)_3$.

As usual, the alkyl derivatives form two isomeric series, derivatives being known of a hypothetical Isomelamine, $(CNH)_3(NH)_3$, among these being the polymerised alkyl-cyanamides.

VII. DERIVATIVES OF CARBONIC ACID

True carbonic acid, $O : C(OH)_2$, is not known in the free state, since two hydroxyl groups cannot exist in combination with the same carbon atom (*see* p. 216), but it is supposed to exist in aqueous solution, and salts corresponding with this formula are stable and well known (carbonates and bicarbonates). Also important organic derivatives, similar to those already studied for other dibasic acids (amides, chlorides, esters, etc.), are known. The acid derivatives are less stable than the normal ones.

ESTERS OF CARBONIC ACID

ETHYL CARBONATE, $CO(OC_2H_5)_2$, is a liquid which is insoluble in water, boils at 126°, and has a pleasant odour. It is formed by the interaction of ethyl chlorocarbonate and alcohol: $C_2H_5 \cdot OH + Cl \cdot CO \cdot OC_2H_5 = HCl + CO(OC_2H_5)_2$, and also from silver carbonate and ethyl iodide. Mixed esters, containing different alkyls, also exist.

ETHYLCARBONIC ACID, $CO(OH) \cdot OC_2H_5$, is known only as salts, *e.g.*, Potassium Ethylcarbonate, $CO(OK) \cdot OC_2H_5$, which is obtained by the action of CO_2 on an alcoholic solution of potassium ethoxide and forms shining scales, giving alcohol and potassium carbonate when treated with water.

CHLORIDES OF CARBONIC ACID

Carbon Oxychloride (*phosgene*), $COCl_2$, has already been described (Vol. I., p. 492).

CHLOROCARBONIC ACID, $COCl \cdot OH$, is the acid chloride of carbonic acid, but is not stable, and, when liberated, decomposes into CO_2 and HCl. Its esters are, however, well known, the action of phosgene on absolute alcohol giving, for example, ethyl chlorocarbonate (Ethyl Chloroformate), $Cl \cdot CO \cdot OC_2H_5$, thus: $C_2H_5 \cdot OH + COCl_2 = HCl + Cl \cdot CO \cdot OC_2H_5$.

This ester is a liquid, having a pungent odour, boiling at 93° and readily decomposing under the action of water; it is used largely in organic syntheses to introduce carboxyl into the molecule.

AMIDES OF CARBONIC ACID

The acid amide, $NH_2 \cdot CO \cdot OH$, is Carbamic Acid, and the normal amide, $NH_2 \cdot CO \cdot NH_2$, *urea*.

CARBAMIC or **CARBAMINIC ACID**, $NH_2 \cdot CO \cdot OH$, is obtained as ammonium salt—*ammonium carbamate*, $NH_2 \cdot CO \cdot ONH_4$—by the direct union of dry CO_2 and NH_3; a white mass is thus obtained which, even at 60°, dissociates into $CO_2 + NH_3$. In aqueous solution this salt does not precipitate solutions of calcium salts at the ordinary temperature, since calcium carbamate is soluble, but in the hot the salt decomposes into CO_2 and NH_3 and gives a precipitate of calcium carbonate.

Ethyl carbamate or **URETHANE**, $NH_2 \cdot CO \cdot OC_2H_5$, is also well known and is obtained by the action of ammonia on ethyl carbonate, $CO(OC_2H_5)_2 + NH_3 = C_2H_5 \cdot OH + NH_2 \cdot CO \cdot OC_2H_5$, or, more easily, by treating ethyl chlorocarbonate with ammonia:

$$COCl(OC_2H_5) + 2NH_3 = NH_4Cl + NH_2 \cdot CO \cdot OC_2H_5.$$

It melts at 48° to 50°, is soluble in water, and is used as a *soporific*.

The following are also known: *iodourethane*, $NHI \cdot CO \cdot OC_2H_5$; *ethylurethane*, $NHC_2H_5 \cdot CO \cdot OC_2H_5$ (boils at 175°); *nitrourethane*, $NO_2 \cdot NH \cdot CO \cdot OC_2H_5$; *carbamidyl chloride*, $NH_2 \cdot CO \cdot Cl$ (melts at 50° and boils at 61°); and *diethyl iminodicarbonate*, $NH(CO \cdot OC_2H_5)_2$, which is the imide of urethane.

Urethane derivatives are readily hydrolysable with alkalis and yield ammonia and urea when heated.

UREA (Carbamide), $CO(NH_2)_2$, is the final oxidation product of nitrogenous compounds in the living organism, and the adult human being produces about 30 grams of it a day; it is found in general in the urine of carnivora (where it was first discovered) and in other animal fluids. It crystallises in shining needles soluble in water and in alcohol, but insoluble in ether; it melts at 132° and sublimes in a vacuum. It is formed from ammonium cyanate by simple rearrangement under the action of heat (Wöhler): $NC \cdot ONH_4 = CO(NH_2)_2$. Escales (1911) found that when urea is distilled or sublimed in a vacuum, the reverse reaction, *i. e.*, formation of ammonium cyanate, occurs. Urea is obtained also by the action of ammonia on ethyl carbonate or carbamic acid:

$$CO(OC_2H_5)_2 + 2NH_3 = 2C_2H_5 \cdot OH + CO(NH_2)_2.$$

Many other reactions give urea, *e. g.*, oxidation of thiourea, action of water on cyanamide, best in the cold and in presence of hydrated manganese peroxide as catalyst (Ger. Pat. 254,474, 1910; U.S. Pat. 796,713); it may also be prepared from $COCl_2$ and NH_3, etc. In the laboratory it is prepared by treating with barium carbonate the urea nitrate obtained by evaporating urine in presence of nitric acid, or by heating ammonium sulphate solution with potassium ferrocyanide or cyanate:

$$(NH_4)_2SO_4 + 2NCOK = K_2SO_4 + 2CO(NH_2)_2.$$

In the future urea will probably be prepared on an enormous industrial scale according to the scheme of the Badische Anilin-und Soda-Fabrik of Ludwigshafen and Oppau. Synthetic ammonia is obtainable by the Haber process (*see* Vol. I., p. 373), and an abundant supply of CO_2 is obtained in the preparation from water-gas of the hydrogen necessary for the synthesis of ammonia. Thus ammonium sulphate may be made economically according to the reaction, $NH_3 + CO_2 + H_2O + CaSO_4 = CaCO_3 + (NH_4)_2SO_4$, and urea from CO_2 and NH_3 in an autoclave: $CO_2 + 2NH_3 = H_2O + CO(NH_2)_2$. Since urea contains more than 46 per cent. of nitrogen, its use as a high-grade nitrogenous fertiliser is anticipated when it can be manufactured to compete with other fertilisers.

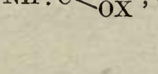
When heated it is decomposed into ammonia, biuret (*see later*), cyanuric acid, and ammelide. It is readily hydrolysed by acids, alkalis, or even hot water: $CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$, and is decomposed by nitrous acid or sodium hypochlorite:

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + 2N_2.$$

Owing to this property urea is used as a stabiliser (so-called!) for explosives, decomposition being retarded and the nitrous vapours fixed (*see* p. 303).

It exhibits the properties of a base and of a weak acid, giving salts with acids (*e. g.*, **Urea Nitrate**, $CO(NH_2)_2, HNO_3$, which is soluble in water and slightly so in nitric acid, and with concentrated sulphuric acid gives the highly acid **Nitrourea**, $NH_2 \cdot CO \cdot NH \cdot NO_2$, and with bases, *e. g.*, $CO(NH_2)_2, 2HgO$. It also crystallises with other salts, *e. g.*, $CO(NH_2)_2 + NaCl + H_2O$, $CO(NH_2)_2 + AgNO_3$, etc. Mercuric nitrate precipitates urea quantitatively from its neutral aqueous solutions as $2CO(NH_2)_2 + Hg(NO_3)_2 + 3HgO$.

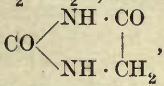
Urea forms various *alkyl derivatives;* thus ethyl cyanate and ethylamine give *symm.* or *a-diethylurea*, which is isomeric with *unsymm.* or *β*-diethylurea, $NH_2 \cdot CO \cdot N(C_2H_5)_2$; $CO \cdot NC_2H_5 + C_2H_5 \cdot NH_2 = CO(NHC_2H_5)_2$. The constitutions of these alkyl derivatives are determined by study of the products of their hydrolysis.

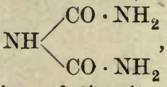


Readily hydrolysable *alkylisoureas*, $NH : C\begin{smallmatrix} NH_2 \\ OX \end{smallmatrix}$, are also known.

SEMICARBAZIDE, $NH_2 \cdot CO \cdot NH \cdot NH_2$, which is obtained from potassium cyanate and hydrazine hydrate, may also be regarded as a derivative of urea. It has already been seen that this base (which melts at 96°) gives crystalline compounds (*semicarbazones*) with ketones and aldehydes (*see* p. 246). **CARBAZIDE** (Carbohydrazide), $CO(NH \cdot NH_2)_2$, melts at 152°, and is obtained from esters of carbonic acid by the action of hydrazine hydrate.

Acetylurea, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CH_3$, and **Allophanic Acid**, $NH_2 \cdot CO \cdot NH \cdot CO_2H$ (not known free, but as salts), are obtained from acid chlorides and urea.

The formation of *ureides* (compounds of urea and mono- and dibasic acids) takes place with monobasic divalent acids or with an alcohol and acid. Such a reaction gives **Hydantoic Acid** (*glycoluric acid*), $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, which, when evaporated in presence of HCl, loses water and forms **Hydantoin**,  $CO\Big\langle\begin{matrix}NH \cdot CO\\ \quad\ |\\ NH \cdot CH_2\end{matrix}$, the latter giving first hydantoic acid and then CO_2, NH_3, and glycine on hydrolysis.

When urea is heated at 160°, 2 mols. condense with separation of ammonia and formation of **Biuret**,  $NH\Big\langle\begin{matrix}CO \cdot NH_2\\ CO \cdot NH_2\end{matrix}$, which crystallises with $1H_2O$ and is soluble in water or alcohol; in alkaline solution it gives a characteristic violet coloration with a little copper sulphate.

DERIVATIVES OF THIOCARBONIC ACID

More or less complete substitution of the oxygen of carbonic acid by sulphur gives a series of unstable compounds, which form stable alkyl derivatives and exhibit various cases of isomerism indicated by varying products of hydrolysis. These numerous sulphur compounds are reducible to three types, according as they contain (1) the nucleus $SC{<}$, *thiocarbonic* or *thiocarbamic compounds*, (2) the nucleus $OC{<}$, *carbonyl* or *carbamic compounds*, or (3) the group $H \cdot N : C{<}$, *iminocarbonic* or *iminocarbamic compounds*.

The following are the principal compounds of these types, which have been thoroughly studied in the form of their alkyl derivatives:

Trithiocarbonic acid . .	$SC(SH)_2$
Dithiocarbonic acid . . .	$SC{<}\begin{matrix}SH\\OH\end{matrix}$
Monothiocarbonic acid . .	$SC{<}\begin{matrix}OH\\OH\end{matrix}$
Dithiocarbamic acid . .	$SC{<}\begin{matrix}NH_2\\SH\end{matrix}$
Dithiocarbonylic acid . .	$CO(SH)_2$
Monothiocarbonylic acid . .	$CO{<}\begin{matrix}SH\\OH\end{matrix}$
Monothiocarbonylamic acid . .	$CO{<}\begin{matrix}NH_2\\SH\end{matrix}$
Monothiocarbamic acid . .	$SC{<}\begin{matrix}NH_2\\OH\end{matrix}$
Thiocarbamide	$SC{<}\begin{matrix}NH_2\\NH_2\end{matrix}$
Thiophosgene. . . .	$SC : Cl_2$
Thiocarbamidyl chloride . .	$SC{<}\begin{matrix}NH_2\\Cl\end{matrix}$
Iminodithiocarbonic acid	$HN : C(SH)_2$
Iminomonothiocarbonic acid	$HN : C{<}\begin{matrix}SH\\OH\end{matrix}$
Iminothiocarbamic acid .	$HN : C{<}\begin{matrix}NH_2\\SH\end{matrix}$

THIOPHOSGENE (Carbon Sulphochloride), $SCCl_2$, is a red liquid which fumes in the air, attacks the mucous membrane, and boils at 68° to 74°. It is prepared by the action of chlorine on carbon disulphide, the intermediate compound, $CCl_3 \cdot SCl$, thus obtained being reduced with stannous chloride. It is more stable towards water than phosgene, and with ammonia gives, not thiourea, but ammonium thiocyanate.

TRITHIOCARBONIC ACID, CS_3H_2, is obtained as sodium salt by the action of carbon disulphide on sodium sulphide. The free acid is a brown unstable oil and its *ethyl ester*, $SC(SC_2H_5)_2$, a liquid boiling at 240°.

POTASSIUM XANTHATE, $KS \cdot SC \cdot OC_2H_5$, is the ether of the potassium salt of dithiocarbonic acid. It is formed by the action of CS_2 on $C_2H_5 \cdot OK$ and crystallises in shining needles soluble in water and to a less extent in alcohol. With copper sulphate it gives copper xanthate as an unstable yellow powder which is used in indigo printing.

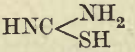
XANTHIC or **XANTHONIC ACID**, $HS \cdot SC \cdot OC_2H_5$, is liberated from its potassium salt (*see above*) and forms an oil insoluble in water; it readily decomposes into $C_2H_5 \cdot OH + CS_2$.

DITHIOCARBAMIC ACID, $NH_2 \cdot SC \cdot SH$, is obtained as ammonium salt by the action of ammonia on an alcoholic solution of CS_2:

$$2NH_3 + CS_2 = NH_2 \cdot SC \cdot SNH_4.$$

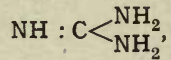
In the free state this acid forms an unstable, reddish oil (decomposing into $SH_2 +$ thiocyanic acid) and its ethyl ester, $NH_2 \cdot SC \cdot SC_2H_5$, is *dithiourethane*, whilst *thiourethane* will be $NH_2 \cdot CO \cdot SC_2H_5$ and is isomeric with *xanthogenamide*, $NH_2 \cdot CS \cdot OC_2H_5$.

Ethylamine Ethyldithiocarbamate, $C_2H_5 \cdot NH \cdot SC \cdot SH, NH_2 \cdot C_2H_5$, is formed similarly by the action of carbon disulphide on ethylamine; in the hot it gives *diethylthiourea*, $SC(NHC_2H_5)_2$, the mercuric salt of which gives the corresponding mustard oil with water in the hot, whilst the alkylated dithiocarbamic acids obtained with secondary amines do not give mustard oils under these conditions.

THIOCARBAMIDE (Thiourea), $SC(NH_2)_2$, is only partly obtained on heating ammonium thiocyanate at 130°, the reaction being reversible. It forms crystals melting at 172°, and dissolving in water and in alcohol, giving neutral solutions; it has a bitter taste. On hydrolysis it yields $CO_2 + H_2S + NH_3$. As has already been stated, it is converted into urea by permanganate, into cyanamide by mercuric oxide, and into potassium thiocyanate and ammonia by alcoholic potash at 100°. It behaves as a weak acid and a weak base, and its derivatives, in some cases, correspond with the tautomeric formula,  $HNC{<}{\substack{NH_2 \\ SH}}$ (hypothetical *iminothiocarbamic acid*).

About 10,000 kilos of thiourea are produced annually by two factories, one French and the other German, for preserving weighted silk from corrosion, the Gianoli process (*see later*, under Silk) being used. Owing to this, the price of thiourea was lowered in pre-war times from £2 to 5*s*. 6*d*. or 6*s*. 6*d*. per kilo.

GUANIDINE AND ITS DERIVATIVES

GUANIDINE (Iminourea or Iminocarbamide),  $NH : C{<}{\substack{NH_2 \\ NH_2}}$, forms crystals readily soluble in water or alcohol. It is a strong base, absorbing carbon dioxide from the air, but is converted into salts by one equivalent of acid. The fatty acid salts are converted on heating into *guanamines*, which form crystals of peculiar shape.

It is obtained by heating cyanamide with ammonium iodide: $NH_4I + CN \cdot NH_2 = NH : C(NH_2)_2, HI$; or, better, as thiocyanate by heating thiourea with ammonium thiocyanate at 190°:

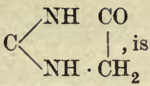
$$NCS \cdot NH_4 + SC(NH_2)_2 = H_2S + NH : C(NH_2)_2, \ NC \cdot SH.$$

It may also be obtained from dicyanodiamide by the action of aqua regia (Ulpiani, 1907).

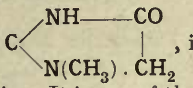
Guanidine is readily hydrolysed, forming first ammonia and urea and then CO_2 and NH_3.

Guanidine Nitrate, $NH : C(NH_2)_2, HNO_3$, is converted by concentrated sulphuric acid into *nitroguanidine*, $NH : C(NH_2)(NH \cdot NO_2)$, and this, on reduction, gives *aminoguanidine*, $NH : C(NH_2)(NH \cdot NH_2)$. The latter gives hydrazine $[(NH_2)_2]$, NH_3, and CO_2 on hydrolysis with acid or alkali, whilst with nitrous acid it yields **Diazoguanidine** (*iminocarbamideazide*), $NH : C(NH_2) \cdot N_3$, which is resolved by alkali into hydrazoic acid (*see* Vol. I., p. 376) and cyanamide.

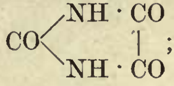
From aminoguanidine can be obtained **Azodicarbonamide**, $NH_2 \cdot CO \cdot N : N \cdot CO \cdot NH_2$, and **Hydrazodicarbonamide**, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$.

GLYCOCYAMINE, $NH : C(NH_2) \cdot NH \cdot CH_2 \cdot CO_2H$, is formed by the union of glycocoll with cyanamide, and if water is lost **Glycocyamidine**,  $NH:C\begin{cases}NH\cdot CO\\ NH\cdot CH_2\end{cases}$, is obtained. If, however, instead of glycocoll, its methyl-derivative is taken, *sarcosine*, $CO_2H\cdot CH_2\cdot NH\cdot CH_3$ (melts at 115° and is neutral), results, *creatine* and *creatinine* being obtained similarly.

CREATINE, $NH:C(NH_2)\cdot N(CH_3)\cdot CH_2\cdot CO_2H$, is obtained from meat-extract, being a stable component of muscle. It has a neutral reaction and is soluble in water and sparingly so in alcohol; it crystallises with $1H_2O$, has a bitter taste and, when heated with acid, loses 1 mol. of water of constitution and forms creatinine; on complete hydrolysis, it gives urea and sarcosine.

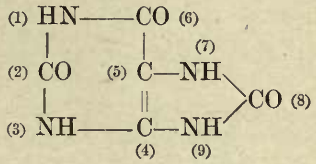
CREATININE,  $NH:C\begin{cases}NH\text{——}CO\\ N(CH_3)\cdot CH_2\end{cases}$, is a weak base and dissolves very readily in water, giving creatine again. It is one of the constituents of urine and forms a characteristic zinc salt, 2 mols. of creatinine combining with 1 mol. of $ZnCl_2$. When hydrolysed, it gives ammonia and methylhydantoin.

URIC ACID AND ITS DERIVATIVES

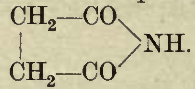
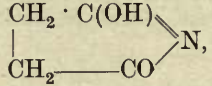
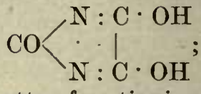
When the two amino-groups of urea condense with the two carboxyl groups of a dibasic acid with expulsion of 2 mols. of water, *ureides* (*see above*) are obtained. Thus, oxalic acid yields *parabanic acid*,  $CO\begin{cases}NH\cdot CO\\ NH\cdot CO\end{cases}$; malonic acid, *barbituric acid*, $CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH_2$; tartronic acid, *dialuric acid*, and mesoxalic acid, *alloxan*, $CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CO$. If, however, only one molecule of water is eliminated, one amino- and one carboxyl-group remaining unchanged, *uro-acids* are obtained, *e.g.*, *oxaluric acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CO_2H$, and *alloxanic acid* (from mesoxalic acid).

These ureides are usually well crystallised, and are aminic and also markedly acid in character. On hydrolysis, they give first the corresponding uro-acid and then urea and free acid. They are sometimes formed on oxidation of diureides (*see below*); thus *parabanic acid* is obtained by oxidising uric acid with nitric acid. The alcohol-acids and the aldehydo-acids also give such condensations (*see above*), yielding, for example, *hydantoin*, *hydantoic acid*, and *allanturic acid* (from glyoxylic acid).

When 2 mols. of urea take part in the condensation, *diureides* are obtained, these forming the group containing uric acid,

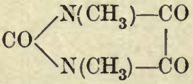


and its derivatives: *xanthine*, *caffeine*, *theobromine*, *guanine*, *hypoxanthine*, *alloxanthine*, *purpuric acid*, *allantoin*, etc. The positions of the substituent groups are indicated by the bracketed numbers shown in the above formula for uric acid. During recent years successful attempts have been made, by means of ethyl cyanoacetate, to synthesise all these xanthine bases and to convert them, one into the other (see *Berichte der deutsch. chem. Gesells.*, 1899, 32, p. 435).

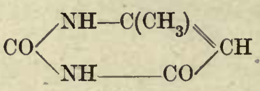
As a general rule, the ureides and diureides have a more or less marked acid character and, as they contain no carboxyl group, this acidity is explained as due to the existence of these compounds in tautomeric forms, just as is the case with *succinimide*,  $\left.\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\right\rangle NH$. In the latter it is assumed that the iminic hydrogen atom is very mobile and undergoes displacement and union with the oxygen of the neighbouring carbonyl group, a double linking between carbon and nitrogen being formed and an acid hydroxyl group capable of forming salts with metals. The tautomeric formula of Succinimide would hence be  $\left.\begin{array}{l}CH_2\cdot C(OH)\\ |\\ CH_2-\!\!-\!\!-CO\end{array}\right\rangle N$, and that of Parabanic Acid,  $CO\left\langle\begin{array}{l}N:C\cdot OH\\ \quad\;\;\, |\\ N:C\cdot OH\end{array}\right.$; similar formulæ hold for *uric acid* and barbituric acid, the latter functioning as a dibasic acid (in this case, however, the acid character is perhaps to be attributed to the hydrogen of the methylene group, CH_2).

Several diureides are found in nature, *e.g.*, in guano, in the urine and muscles of carnivora, in the excreta of serpents, in articular concretions, and in certain plants (theobromine in cocoa, caffeine, etc.).

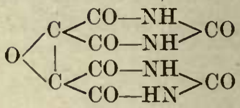
The constitutional formulæ of the more important diureides are as follow:



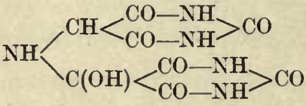
Dimethylparabanic acid
(Cholestrophane)



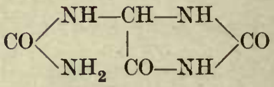
Methyluracil



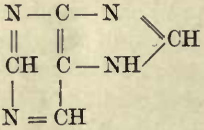
Alloxanthine



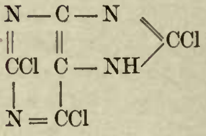
Murexide



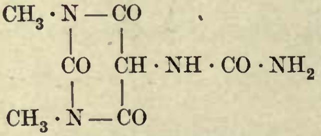
Allantoin



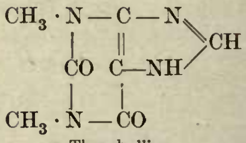
Purine



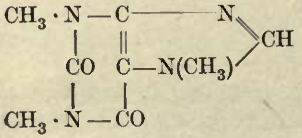
Trichloropurine



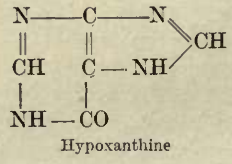
Dimethylpseudouric acid



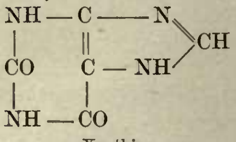
Theophylline



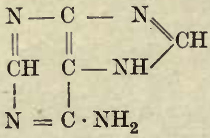
Caffeine



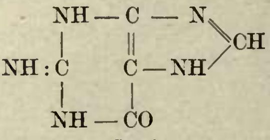
Hypoxanthine



Xanthine

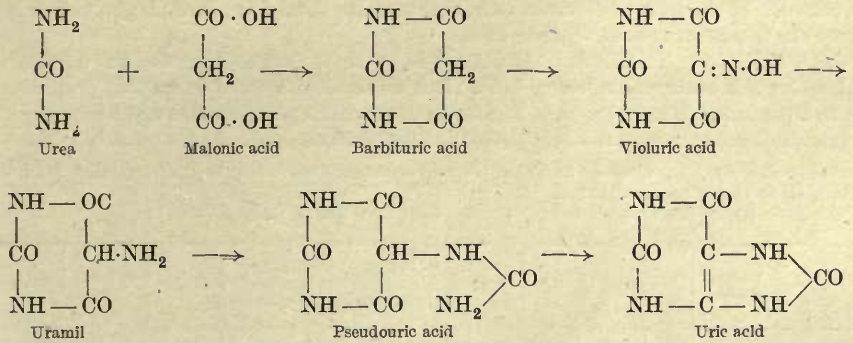


Adenine



Guanine

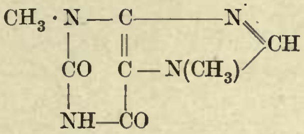
URIC ACID, $C_5H_4O_3N_4$. Syntheses of uric acid are many and various; from cyanoacetic acid, or glycocoll or isodialuric acid, by heating with urea; from aminobarbituric acid and potassium cyanate; from ethyl acetoacetate and urea, passing through methyluracil, nitrouracil, hydroxyuracil, and isodialuric acid. The following scheme represents the various steps of the synthesis from malonic acid:[1]



Uric acid is a feeble dibasic acid (*see above*), and forms a white, amorphous substance insoluble in alcohol or ether and almost insoluble in water. It dissolves, however, in concentrated sulphuric acid, from which it separates unchanged on dilution with water. It is extracted from guano, the excrements of serpents, and the urine of carnivora.

Evaporation of uric acid with dilute nitric acid and treatment of the residue with ammonia yields *murexide*, which forms yellowish green crystals which give a purple aqueous solution, turning blue on addition of alkali (characteristic reaction for uric acid).

THEOBROMINE (3 : 7-Dimethyl-2 : 6-dioxypurine), $C_7H_8O_2N_4$ or



is extracted by means of boiling alcohol from *cocoa*,[2] de-fatted and made into a paste with

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[1] The *constitution of uric acid* was demonstrated first by Medicus, and later, by various syntheses, by E. Fischer (Liebig's *Annalen*, 1882, 215, p. 253). The presence of a chain, —C—C—C—, and of a carbonic acid residue is shown by the formation of urea and alloxan when uric acid is treated in the cold with nitric acid. The presence of four imino-groups is deduced from the fact that, by introduction of four methyl groups and subsequent hydrolysis, the four atoms of nitrogen are eliminated as methylamine. A large part of the uric acid molecule is rendered evident by the formation of allantoin (of known constitution) on oxidation with alkaline permanganate, and by the formation of methylurea and methylalloxan on oxidation of dimethyluric acid.

[2] **Cocoa and Chocolate.** Cocoa is placed on the market in the form of large violet seeds of *Theobroma cacao*, which grows well in the Antilles, Mexico, Guatemala, Java, Borneo, Esmeralda (equator), etc. The red or brown mature fruits resemble cucumbers, each containing fifty to sixty seeds like beans. The seeds are separated from the pulp, heaped in casks for four to five days to initiate the fermentation which increases the aroma, and then dried in the sun. The chemical composition of the decorticated seeds differs considerably with the variety: fatty substance (*cocoa-butter*), 40 to 55 per cent.; proteins, 10 to 18 per cent.; cellulose, 3 to 6 per cent.; sugars and starch, 8 to 15 per cent.; theobromine, 0·8 to 2·5 per cent.; ash, 3 to 4 per cent. *Cocoa-butter* (or cacao-butter) is extracted by pressing the seeds hot, and forms a faintly yellow mass of pleasing odour; it melts at 29° to 31°, and contains the glycerides of arachic, palmitic, oleic, stearic, and lauric acids.

In the manufacture of chocolate, the seeds are washed in suitable sieves and then gently and cautiously heated for thirty to forty minutes to facilitate skinning. They are next crushed in mortars or rotating cylinders, the flour obtained being made into a paste with sugar and worked for a long time on heated stone rollers, different ingredients and flavouring matters being added to give the different kinds of chocolate; the homogeneous paste then passes to the moulds.

lime. Synthetically it is obtained by treating the lead salt of xanthine with methyl iodide, or from methyluric acid and phosphorus oxychloride. It forms white, anhydrous crystals which have a bitter taste and dissolve only slightly in water, alcohol or ether. It is soluble in acids or alkalies, and at 290° volatilises without melting. It behaves as a weak acid and as a weak base. With methyl iodide the silver salt yields *caffeine*. With concentrated nitric acid, chlorine and ammonia, it gives the same reactions as caffeine (*see below*). In the form of different salts, theobromine is used as a stimulant and diuretic. Before the war it cost about 72*s*. per kilo.

CAFFEINE or **THEINE**, $C_5H(CH_3)_3O_2N_4 + H_2O$, is *trimethylxanthine* or *methyltheobromine* (for constitution, *see* p. 436). It is an alkaloid formed in varying proportions (0·5 to 2 per cent.) in *coffee* seeds.[1] The leaves of the coffee plant contain up to 1·3 per cent.,

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Good chocolate contains from 40 to 60 per cent. of cocoa, the rest being sugar; ordinary qualities contain 10 to 15 per cent. of starch.

The amounts of cocoa imported by various countries are as follows (tons):

	United States	Germany	Great Britain	France	Holland (one half re-exported)	Belgium (one half re-exported)	Spain	Switzerland	Italy
1907 .	39,239	34,515	25,900	23,180	22,870	5,963	5,652	7,124	1,456
1910 .	52,546	43,941	32,046	25,076	34,229	9,881	5,517	9,089	1,886
1912 .	69,447	55,085	34,145	26,890	41,858	13,023	5,241	10,342	2,432
1913 .	70,660	52,878	35,543	27,610	46,810	11,620	6,166	10,248	2,457
1914 .	80,479	—	42,416	26,085	52,375	—	6,911	10,078	2,275
1916 .	110,050	—	90,237	37,172	21,112	—	7,504	14,705	6,746
1918 .	—	—	—	—	—	—	—	—	5,863

The cocoa crop in the British colony of the Gold Coast increased from 5770 tons in 1904 to 40,640 tons in 1911; in the German colonies, especially the Cameroons, the crop rose from 1454 tons in 1905 to 5500 tons in 1912.

Italy imported and exported the following quantities of *chocolate*:

		1908	1910	1913	1914	1916	1918
Importation	Tons .	1,090	1,500	2,078	1,627	876	211
	Value, £ .	—	180,000	216,160	—	—	59,120
Exportation	Tons .	230	230	273	308	362	336
	Value, £ .	—	30,704	—	38,266	69,544	107,584

Before the war the price of cocoa was about £4 per cwt.

[1] Coffee consists of the seeds of one of the Rubiaceæ (*Coffea arabica*) which grows naturally in Southern Ethiopia and Arabia, and is cultivated on an enormous scale in India, the Antilles, Madagascar, and South America. It is an evergreen plant, 6 to 9 metres high and of pyramidal habit, with greyish branches and lanceolated leaves, the flowers (at the base of the leaf) being white and pleasant-smelling, like jessamine. The fruit forms drupes like cherries, the epicarp passing from yellow to green to red to brownish, and the mesocarp being yellow, pulpy and of agreeable taste. The endocarp is divided into two compartments surrounded by coriaceous membrane and each containing a seed, which has one convex and one flat, furrowed face, and is covered by a friable pellicle; the endosperm (albumen) is yellowish or greenish and horny.

Coffee berries are composed of cellulose (18 per cent.), fatty matters (12 per cent.), gummy and saccharine substances (10 per cent.), nitrogenous compounds (12 per cent.), mineral salts (4 to 5 per cent.), a tannin (*caffetannic acid*, 8 per cent.), caffeine (0·8 to 1·3 per cent.), *caffearine*, and water (11 per cent.). When roasted, coffee develops aroma and loses 15 to 20 per cent. in weight, but increases in volume by one-third, while the sugar caramelises and the cellulose carbonises partially, forming a brown oil which is denser than water, dissolves in ether, and constitutes the aromatic substance (*caffeone*). *Roasted coffee* contains, on the average, 1·5 per cent. of water, 13 per cent. of nitrogenous substances, 0·8 per cent. of sugars, 13·5 per cent. of fats, 4·8 per cent. of ash, 0·9 per cent. of caffeine, and 46 per cent. of non-nitrogenous substances; to hot water this coffee gives up about 25 per cent. of its weight.

The form of the seed varies with the kind of the coffee (*Coffea mauritiana, laurina, liberica, etc.*). Mocha coffee berries are small and the Australian ones large, whilst those from the Antilles are intermediate in size.

The quality of coffee is influenced by the methods of cultivation and preparation: by the ordinary or *dry* method the fruit is dried in the sun, so that it may be freed from the parchment-like membrane and partly from the silvery pellicle by beating in a husking machine. In the West Indies and Brazil, however, more use is now made of the *wet process*, in which the fresh fruit is carried by a stream of water into a de-pulping machine fitted with revolving channelled or toothed discs or cylinders, the seeds after this treatment being covered only with the parchment integument and with a little pulp, which is eliminated by fermentation and subsequent washing; finally the seeds are dried in the sun or in an oven, and may then be freed from the parchment by decorticating machines. One hundred kilos of fresh fruit gives about 20 kilos of berries for sale, these being rendered shiny by shaking them dry in sacks or in levigating apparatus, in which finely powdered colouring matters (indigo, ultramarine, chromium salts, curenin, graphite, etc.) are often introduced.

The cultivation of coffee has received a considerable impulse in Brazil, where as much as 800,000 tons (more than three-fourths of the total production of the world) is now produced. Of the Antilles coffees, the most highly valued is that from Porto Rico. The principal commercial varieties of coffee are named after the countries where they are grown. The output in different countries is as follows (tons):

	Brazil	Other American countries	Asia and Oceania (except Arabia)	Africa and Arabia	Whole world
1900–1901 .	675,700	170,000	46,100	11,300	910,000
1904–1905 .	632,000	181,400	39,500	8,200	861,000
1909–1910 .	1,150,000	36,000	26,000	1,500 (?)	1,300,000
1913–1914 .	680,000	85,000	36,000	1,000 (?)	850,000 (?)

In 1902 the mean consumption per head in kilos amounted to: Holland, 6·6; Norway, 5·3; Sweden, 5·2; United States, 5·1; Belgium, 4·7; Denmark, 3·4; Germany, 3; France, 2·2; Austria, 0·9; Italy 0·5; Spain, 0·5; Great Britain, 0·43.

The total importation is as follows (tons):

	Germany	Great Britain	France	Belgium (one-third re-exported)	Holland (two-thirds re-exported)	United States	Italy	Spain
1907	189,600	53,596	101,570	113,350	117,857	426,487	21,476	11,292
1910	171,000	47,600	112,000	50,000	120,000	364,876	25,287	12,838
1912	171,000	34,200	111,240	50,000	116,250	427,516	27,627	13,378
1913	168,000	43,000	115,280	53,480	144,950	387,000	28,659	15,129
1914	—	52,680	116,420	—	124,950	458,620	28,197	13,733
1916	—	82,880	153,000	—	89,000	529,297	48,961	16,383
1918	—	—	—	—	—	—	51,638	—

In 1900 Italy imported 14,100 tons of coffee, in 1908 22,760, and in 1910 25,300 tons (£1,062,080) (about four-fifths from Brazil); the Customs' duty was £60 per ton until 1909, after which it was lowered somewhat. Pre-war prices per cwt. at Genoa, exclusive of duty, were: Mocha, £4; Porto Rico, 72*s.*; Peru, 50*s.*; Salvador, 56*s.*; San Domingo, 44*s.* (washed 60*s.*); Santos, 42*s.*; Rio, 38*s.*; Bahia, 36*s.*

In 1909, coffee became a State monopoly in Italy, the retail price being raised in January, 1920, to 14*s.* to 17*s.* (18 to 22 lire) per kilo, according to the quality; before the war, the price was 3*s.* 6*d.* to 4*s.* 6*d.* (including 1*s.* 2*d.* duty).

Coffee Substitutes. These are now numerous, and as a rule contain no caffeine, being obtained by roasting roots, saccharine fruits, cereals, leguminous seeds, etc. On roasting, the saccharine substances form caramel and other bitter substances giving colour, taste and smell to the aqueous decoction. Chicory coffee contains, on the average: water, 8 per cent.; nitrogenous substances, 7; fats, 2·5; sugar, 16; non-nitrogenous extractives, 52 (9 per cent. induline and 12 per cent. caramel); cellulose, 10, and ash, 5 per cent.; about 65 per cent. is soluble in water.

Beet coffee, carrot coffee, etc., are also sold, and in Germany and Austria large quantities of fig coffee are used, this being often mixed with coffee made from dates, carobs, lupins, wheat, rye, barley, maize, malt, acorns, chestnuts, arachis nuts, etc.

These substitutes may be distinguished from coffee by microscopic examination, by their small proportion of fat (1 to 3 per cent., whereas coffee contains up to 14 per cent.), and by the high content of saccharine substances (3 to 50 per cent., while coffee contains 2 per cent. at most).

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larger proportions occurring in the leaves of the tea plant (1·2 to 4 per cent.),[1] in cola nuts (2 to 3 per cent.), in maté leaves (or Paraguay tea; about 1 per cent.) and in guarana paste (made from the seeds of *Paullinia sorbilis*, grown in Brazil: 3 to 5 per cent.).

[1] Tea is an evergreen shrub (*Thea viridis*, *Thea bohea*, and *Thea assamica*), cultivated in China, Japan, British India, Java, Ceylon, and Brazil. The leaves are similar to those of the white willow, and contain various enzymes, of importance being an oxydase which, under suitable conditions of temperature and moisture, transforms the green matter into a black substance (the tannins being oxidised). The oxydase is more sensitive to heat than other enzymes producing the aroma, so that if the leaves are heated for more than an hour at 70° for green tea or at 80° for black tea, the maximum aroma is developed, while the tannin (oxidised) and theine (volatilised) are diminished in amount and the soluble substances increased (Sawamura, 1912). For *black tea*

Industrially caffeine may be extracted from coffee, tea, or maté leaves, in which it is partly combined with tannic acid, by decomposing the compound with water and then treating with chloroform, which readily dissolves it (from coffee it may be extracted directly with benzene, which takes out the oil also; after evaporation of the benzene, the caffeine is separated by means of water, the oil remaining insoluble). Tea residues may be extracted directly with solvents such as alcohol, previous pulping with lime (as used in the case of guarana paste) not being always necessary. During the war a certain amount of caffeine was obtained in Italy by extraction of the soot deposited in the flues of the apparatus used for roasting coffee.

Synthetically caffeine may be prepared by methylating 3-methylxanthine, 1 : 7-dimethylxanthine (paraxanthine) or 3 : 7-dimethylxanthine (theobromine) by means of methyl iodide and caustic soda.

Pure caffeine forms white, silky, odourless needles of bitter taste; at 100° it loses the molecule of water of crystallisation, and it sublimes readily and melts at 228° to 230°. It dissolves readily in chloroform, to some extent in boiling water, slightly in alcohol or cold water, and very slightly in ether. It dissolves in acids forming unstable crystallisable salts. When heated gently to dryness with a little chlorine water and concentrated nitric acid, it leaves a reddish-yellow residue which gives a purple-violet coloration with a little ammonia. Before the war it cost £2 per kilo, but during the war it was sold in Italy at £12 (300 lire) per kilo.

GUANINE, $C_5H_5ON_5$ (constitution given above), is a di-acid base, but forms salts also with bases. It is a white powder insoluble in water but soluble in ammonia. On oxidation with potassium chlorate and hydrochloric acid, it gives carbon dioxide, parabanic acid, and guanidine.

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the leaves are allowed to wither and soften in the sun, and are then rolled up and covered with moist cloths to accelerate the fermentation, which transforms the green into black substances. Rolling of the leaves results in rupture of the cells and expression of the juice which facilitates the fermentation; when the latter ceases (in a few hours) the material is spread either on iron plates heated over direct fire or on gratings heated with hot air (not over 80°). To prepare *green tea*, the withered leaves are subjected to rapid treatment with boiling water or steam to destroy the oxydase (the enzymes producing the aroma are more resistant), so that the green colour may be preserved. The prepared tea is kept in sealed boxes of metal foil, in order that extraneous odours may not be absorbed.

From 4 kilos of leaves 1 kilo of dry tea is obtained. Commercially the numerous varieties are grouped into three types: green, black, and scented, the last two being slightly fermented. The active alkaloid is Theine (*see above*). The best infusion of tea is obtained by macerating for thirty minutes in cold water and then adding boiling water, the liquid being poured off before it becomes very brown and excessively rich in tannin (20 grams of tea per litre of slightly hard water).

The *world's output* of tea is about 600,000 tons, and is furnished almost entirely by Asia [55 per cent. from China and the rest from India (120,000 tons), Ceylon (85,000 tons), Japan (28,000 tons), Formosa, and Java].

The consumption of tea in different countries is shown by the following amounts imported (tons):

	Great Britain (one-sixth re-exported)	Russia	United States	France	Holland	Belgium (two-thirds re-exported)	Spain	Italy
1907	143,846	92,856	44,959	1,155	4,174	766	143	74
1910	150,522	70,172	44,501	1,261	4,970	749	156	74
1912	163,771	68,509	44,772	1,309	5,508	1,051	187	87
1913	165,580	78,513	40,378	1,207	5,467	586	214	95
1914	168,705	78,271	44,466	1,980	6,461	—	122	75
1916	171,306	78,400	47,522	2,645	8,185	—	202	106

Other imports were in 1913 (tons): Canada, 16,300; Austria, 2,000; Denmark, 467; Roumania, 350; Switzerland, 528; Argentine, 1880; Chili, 1746; Persia, 4770, and Australia, 16,940.

Before the war, tea was sold in Italy at 3*s*. to 6*s*. per kilo (including the import duty of 2*s*.), according to the quality.

XANTHINE, $C_5H_4O_2N_4$ (constitution given above), is a white powder and acts as both acid and base. It is obtained from guanine by the action of nitrous acid, and its lead salt reacts with methyl iodide, giving theobromine.

ADENINE, $C_5H_5N_5$ (constitution given above), forms shining needles and is a base occurring in tea and in ox-pancreas. It is formed by decomposition of the nuclein of the cell-nuclei and is hence of physiological importance.

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